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Highly Versatile Synthetic Approach to Oligopyridines and Derivatives by Kröhnke−Type Ring−Closure Reactions

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Dedicated to Professor Michael Hanack on the occasion of his 80th birthday

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The synthesis of a large variety of different conjugated oligopyridines and derivatives with electron poor and/or rich peripheral substituents and with pyridine and other (hetero)aromatic cores by the highly versatile Kröhnke-type synthesis is described. Simple electronic and steric considerations of the participating unsaturated ketones (chalcones) allow a rough estimation of the synthetic accessibility of the desired compounds.

Keywords: Pyridine, ring-closure reaction.

Introduction

The control over structures on the nanoscale is a central issue in the field of nanosciences. The highly attractive bottom-up approach to nanostructures requires carefully tailored building blocks, which self-assemble into the desired architectures. The properties of the self-assembled arrays emerge from the functionalities delivered by the functional molecular building blocks. Thus, there is a need for highly versatile molecules, which fulfill all the requirements as self-assembling building blocks. The class of oligopyridines is predestined for these purposes.[1] Such compounds are synthetically easily accessible, structurally variable, chemically and thermally stable, can planarize upon adsorption on flat surfaces, and act as ligands for metal complexation and as hydrogen bond donors and acceptors.

There is a vast variety of synthetic strategies to access oligopyridines either by metal catalyzed coupling or by ring-closure reactions. Despite the high versatility of the (cross) coupling reactions, especially the longer oligomers are hardly accessible through this route as intermediate compounds in the course of the reaction suffer sufficient solubility. In contrast, non-cyclic precursor molecules for ring-closure reactions offer good solubilities in combination with accessibility and variability. Several strategies were described in the literature from which a few shall be presented in the following. The reaction of pyridyl substituted glyoxyl aldehyde with pyridineamidrazones leads to the formation of 1,2,4-triazines, which are transformed in a [4+2] cycloaddition by the elimination of nitrogen to the corresponding oligopyridines.[2] Potts and coworkers developed a synthetic route of alkylthio substituted oligopyridines by the reaction of acetyl pyridines with α-oxoketene dithioacetals.[1d,3] Already in the sixties of the last century Kröhnke reported the synthesis of oligopyridines from pyridinium salt activated methyl ketones and α,β-unsaturated ketones or related compounds.[4]

In the past ten years we have described the synthesis and self-assembly properties of C_{2v} symmetric bis(terpyridine) derived oligopyridines with a pyrimidine core, the so-called **BTPs** (Figure 1a).[5] These **BTPs** are formed from a double Kröhnke-type reaction of the bispyridinium salt of bisacetyl phenylpyrimidine with (hetero)aromatic unsaturated ketones (chalcones). In total there are five isomers of the **BTPs** known (**2,3'-**, **2,4'-**, **3,3'-**, **4,3'-**, and **2,2'-BTP**).[5] These compounds possess an internal (hetero)aromatic ring system and four peripheral pyridine rings. While the central moiety determines the symmetry and relative orientation of the peripheral pyridine rings, the peripheral units display highly specific[6] intermolecular C-H···N hydrogen bonding interactions with neighboring molecules in, *e.g.*, two-dimensional (2D) arrays. The different isomers self-assemble into a broad variety of different 2D structures on various substrates like highly ordered pyrolytic graphite (HOPG) or Au^{III} at the liquid|solid and gas|solid interface, respectively.[5a,5c,7] The number of synthetically accessible **BTP** isomers via the double Kröhnke-like ring-closure reaction is limited because of the limited number of dipyridylchalcones. These limitations could be mostly bypassed by substituting the central pyrimidine core of the **BTPs** with a corresponding pyridine unit resulting phenylseptipyridines (**PhSpPys**). By this strategy further isomers with self-assembly behavior corresponding to three missing **BTP** isomers could be obtained.[5d] The rich 2D phase behavior makes this class of C_{2v} symmetric oligopyridines highly attractive and rises the question if further structural modification of the molecules is possible to even extend that class.

In the following, we show that the Köhnke-like approach can be quite generally exploited by introducing other substituents in the periphery than pyridine and by substitution of the core unit by other (hetero)aromatic moieties, respectively. Such compounds display different shapes, symmetries and peripheral functionalities by keeping

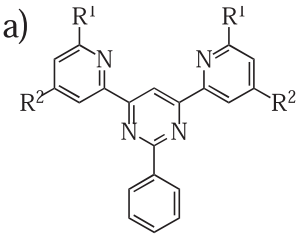
the coplanarity and mostly the hydrogen bonding capability with the perspective of forming highly ordered 2D arrays.

Results and Discussion

The already described synthesis of oligopyridines in a double Kröhnke-type reaction with a pyrimidine[5a,5c] and a pyridine[5d] core (Figure 3), respectively, can be extended to obtain further C_{2v} symmetric (hetero)aromatic compounds (Figure 1). On one side, the peripheral ring systems can be broadly varied but also the core moiety can be exchanged by further (hetero)aromatic units. The periphery of those molecules determines the intermolecular interactions in self-assembled arrays like 2D monolayers whereas the core unit steers the overall geometry of the molecules. By changing the pyrimidine core by a pyridine unit the relative orientation of the coupled pyridine rings is inverted because of the energetically favourable N-N transoid conformation (Figure 3). In both systems the relative orientation of the pyridine units formed by ring closure is 120° whereas *para*-substitution[4] forces the rings in a 180° alignment resulting the so-called bar-bell compounds (**BBC**). If the central moiety of the **BBCs** contains nitrogen atoms like in pyrazine the planarization of the whole system is favoured with the peripheral rings in transoid conformation whereas pyridazine as core unit favours the cisoid conformation (Figure 4). In addition, further substituents at the core units like phenyl rings enhance the solubility but affect also the self-assembly properties of the resulting oligomers by, *e.g.*, π-π stacking. Thus, a subtle interplay between intramolecular constitution and conformation influence the molecular and supramolecular structures.

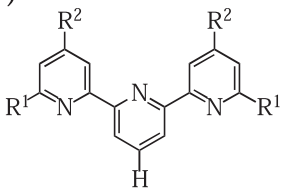
Besides those structural effects the synthetic feasibility of these compounds is crucial for their application as (self-assembling) materials. The success of the Kröhnke pyridine synthesis strongly depends on the substituents of the

a)



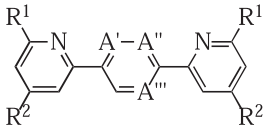
	R^1	R^2
(2N,Ph'-BTP)	2-py	Ph
(2N,3S'-BTP)	2-py	3-th
(3S,2N'-BTP)	3-th	2-py
(2N,sty'-BTP)	2-py	sty
(3N,sty'-BTP)	3-py	sty

b)



	R^1	R^2
(2,3'-SpPy)	2-py	3-py
(2,4'-SpPy)	2-py	4-py
(4,3'-SpPy)	4-py	3-py
(2,5,3'-SpPy)	pyz	3-py
(2N,3S'-SpPy)	2-py	3-th
(3S,2N'-SpPy)	3-th	2-py
(2N,2S'-SpPy)	2-py	2-th
(3N,3S'-SpPy)	3-py	3-th
(3S,3N'-SpPy)	3-th	3-py
(3S, Ph'-SpPy)	3-th	Ph
(Ph,3S'-SpPy)	Ph	3-th
(3OH,2N'-SpPy)	3-hy	2-py
(3OH,4N'-SpPy)	3-hy	4-py
(BiPh,BiPh'-SpPy)	BiPh	BiPh
(Ph,BiPh'-SpPy)	Ph	BiPh
(4Br,Ph'-SpPy)	4-Br	Ph
(4F,Ph'-SpPy)	4-F	Ph
(2N,4F'-SpPy)	2-py	4-F
(2S,2S'-SpPy)	2-th	2-th
(2S,3S'-SpPy)	2-th	3-th
(3S,2S'-SpPy)	3-th	2-th
(3S,3S'-SpPy)	3-th	3-th
(BiPh,Ph'-SpPy)	BiPh	Ph
(2N,Sty'-SpPy)	2-py	sty
(3,Sty'-SpPy)	3-py	sty
(Ph,Sty'-SpPy)	Ph	sty
(3N,P'-SpPy)	3-py	P

c)



	R^1	R^2	A'	A''	A'''
(2N,Ph'-Ph-BBC)	2-py	Ph	CH	CH	CH
(Ph,3N'-Ph-BBC)	Ph	3-py	CH	CH	CH
(3,3'-Ph-BBC)	3-py	3-py	CH	CH	CH
(2,3'-Ph-BBC)	2-py	3-py	CH	CH	CH
(4,3'-Ph-BBC)	4-py	3-py	CH	CH	CH
(Ph,Ph'-Pdz-BBC)	Ph	Ph	N	N	CH
(2,2'-Pdz-BBC)	2-py	2-py	N	N	CH
(Ph,Ph'-Pyz-BBC)	Ph	Ph	N	CH	N
(3,3'-Pyz-BBC)	3-py	3-py	N	CH	N

Figure 1. Overview on the oligopyridine systems newly synthesized: a) bis(terpyridine) derived oligopyridines (**BTPs**), b) septipyridines (**SpPys**, R^3 = H), and c) bar-bell compounds (**Ph-BBC**, $A^1 = A^2 = A^3$ = CH; **Pdz-BBC**, $A^1 = A^2$ = N, A^3 = CH; **Pyz-BBC**, A' = A''' = N, A'' = CH) (for abbreviations see footnote of Table 1).

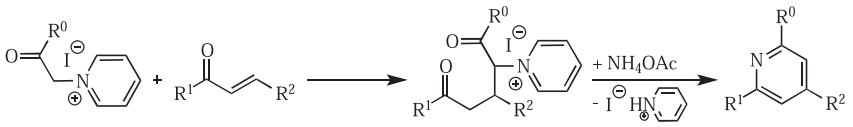


Figure 2. Mechanism of the Kröhnke pyridine synthesis.[4]

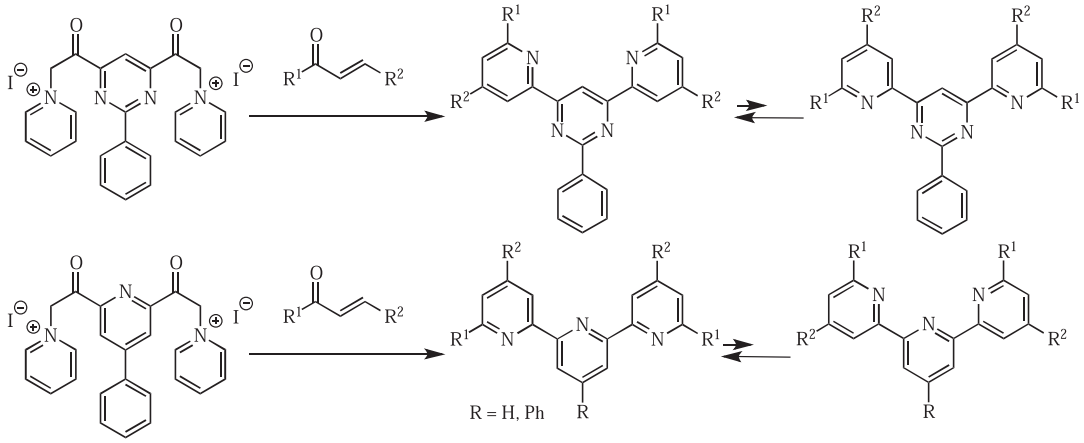


Figure 3. Synthetic pathway to the bis(terpyridine) (**BTP**, top), the phenylseptipyridine (**PhSpPy**, bottom) and the septipyridine (**SpPy**, bottom) based backbone systems in the preferred and less preferred conformation (R^1, R^2 see Figure 1).

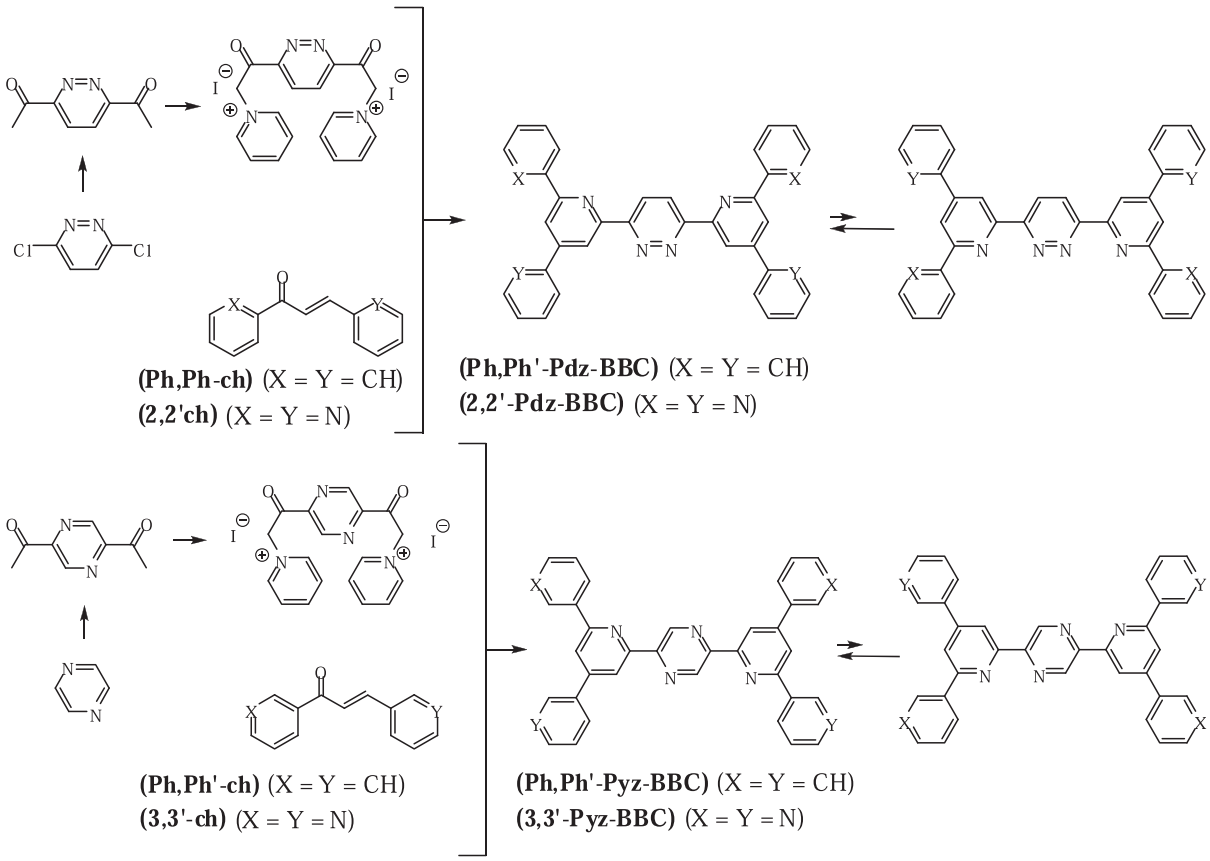


Figure 4. Synthetic pathway to pyridazine (**Pdz-BBC**, top) and pyrazine (**Pyz-BBC**, bottom) bar-bell compounds in the preferred and less preferred conformation.

pyridinium salt and the α,β-unsaturated ketone (chalcone) (Figures 2-4). In the first key step the pyridinium activated methylene group attacks the double bond of the chalcone in a Michael addition and in the second step aza ring closure is provided by ammonium acetate.[4] Those steps require sufficient nucleophilicity of the methylene group and electrophilicity at the carbonyl C and the β-C atom of the chalcone.

Efficient synthesis requires high purity compounds in acceptable yields. Furthermore, the yields may give some insight to the reactivity of the involved components. In the present report they fluctuate between almost 80% and below

1% depending on the different chalcones and bispyridinium salts (Table 1). It should be noted that the ring closure has to take place twice for each compound, *i.e.*, the yields for the single ring closure step vary between 88 and 5% assuming independent reaction steps in the molecules. Furthermore, the values after workup are given, thus, different losses not related to reactivity but, *e.g.*, to solubility will have a significant influence on the yields, too.

The average yields of the different bispyridinium salts are found in three groups with 40-50% (**BTP**, **Ph-BBC**), around 20% (**PhSpPy**, **SpPy**, **Pdz-BBC**), and 5% yield (**Pyz-BBC**). We assume that those differences are caused by the stability of the respective salts, *i.e.*, the decrease of the yields in the row pyrimidine > pyridazine > pyrazine could originate from decomposition of the starting materials or intermediate products under the reaction conditions. As the byproducts were not further analyzed we do not have a clear proof of this assumption.

In order to derive a statistically more reliable relation between the yields and the substituents of the participating chalcones a maximum number of reactions between different chalcones with a certain bispyridinium salt should be investigated. As seen in Table 1, the reactions of the **SpPy** bispyridinium salt led to 28 oligomers, which will be looked at more in detail. In the low yield region below 10% mainly thienyl, phenyl, biphenyl, styryl, hydroxyphenyl, and pyrenyl are employed as substituents whereas higher yields are obtained for 2-pyridyl, 4-pyridyl, and pyrazinyl containing chalcones. Especially, the 2-pyridyl substituent guarantees high yields in the Kröhnke-type reaction. This finding is attributed to the withdrawing effect of the electron

Table 1. Yields of the ring closure reactions with the different bispyridinium salts.

R[1 a]	R[2 a]	Yield /%	R[1 a]	R[2 a]	Yield /%
		BTP			**SpPy**
3py	sty	2	3th	3py	10
3py	3py	13[5c]	3th	Ph	10
2py	3th	15	4F	Ph	11
2py	Ph	18	3th	2th	14
Ph	Ph	24	2py	3py	18
2py	sty	43	2py	sty	28
2py	2py	62[5d]	3th	3th	31
4py	3py	69[5c]	4py	3py	32
2py	3py	70[5c]	pyz	3py	33
2py	4py	71[5c]	3hy	2py	35
3th	2py	71	3th	2py	35
	avg. yield	42	2py	3th	35
		PhSpPy	2py	4F	36
2py	4py	11[5d]	2py	4py	53
2py	3py	16[5d]	2py	2th	53
3py	3py	17[5d]	BiPh	BiPh	58
pyz	3py	20		avg. yield	19
2py	2py	26[5d]			**Ph-BBC**
4py	3py	38[5d]	3py	3py	18
	avg. yield	21	2py	3py	35
		SpPy	2py	Ph	54
2th	2th	0.3	Ph	3py	74
3th	sty	0.9	4py	3py	79
2th	3th	0.9		avg. yield	52
Ph	3th	1.2			**Pdz-BBC**
3py	P	2	Ph	Ph	20
3py	3th	3	2py	2py	27
3hy	4py	5		avg. yield	24
Ph	sty	5			**Pyz-BBC**
4Br	Ph	6	Ph	Ph	3
3py	sty	7	3py	3py	6
BiPh	Ph	8		avg. yield	5
Ph	BiPh	9			

[a] 2py: 2-pyridyl, 3py: 3-pyridyl, 4py: 4-pyridyl, 2th: 2-thienyl, 3th, 3-thienyl, Ph, phenyl, pyz: pyrazinyl, 3hy: 3-hydroxyphenyl, P: pyrenyl, 4Br: 4-bromophenyl, 4F: 4-fluorophenyl, BiPh: biphenyl.

poor nitrogen comprising heteroaromatics, which favor the nucleophilic attack in the Michael addition and in the ring closure. Interestingly, 3-pyridyl substituted chalcones display rather poor yields not only for the **SpPys** but also for the **BTPs** and **BBCs**. Here, the relatively higher electron density in 3-position of the pyridine ring disfavors the desired nucleophilic reaction as already found for the synthesis of the chalcones.[5d] The comparably high yields of the bis(3-thienyl) and bis(biphenyl) substituted oligomers are regarded as exception, which might be caused by solubility effects in the workup. Corresponding results are found for the other bispyridinium salts, too, including the oligopyridines, which we have prepared recently[5c,5d] (Table 1).

It shall be noted that besides electronic effects sterics play an important role, too. Thus, further sterically demanding chalcones with anthracene and/or pyrene substituents were prepared (see experimental section). Attempts to convert those chalcones with the aforementioned bispyridinium salts to the corresponding oligomers were not successful.

Conclusion

We have shown that a broad variety of different chalcones can be reacted with bispyridinium salts to yield oligopyridines with different electron poor and/or rich substituents. The accessibility of those compounds can be fairly predicted by simple electronic considerations at the chalcones. Further investigations on the two-dimensional self-assembly properties of these compounds are ongoing.

Experimental

General

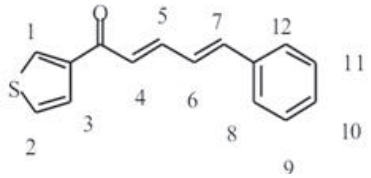
The used chemicals were obtained from commercial sources, all at least with a purity of 96% and they were used without further purification.

The following chalcones and bispyridinium salts were synthesized according to the literature: bisphenyl chalcone **(ch)**, 2-pyridyl-2'-thienyl chalcone **(2N,2S'-ch)**, 2-pyridyl-3'-thienyl chalcone **(2N,3S'-ch)**, 3-pyridyl-3'-thienyl chalcone **(3N,3S'-ch)**, 2-thienyl-2'-thienyl chalcone **(2S,2S'-ch)**, and 2-thienyl-3'-thienyl chalcone **(2S,3S'-ch)**,[8] 2-pyridyl-2'-pyridyl chalcone **(2,2'-ch)**, 2-pyridyl-phenyl chalcone **(2N,Ph'-ch)**, and phenyl-3'-pyridyl chalcone **(Ph,3N'-ch)**,[9] 2-pyridyl-3'-pyridyl chalcone **(2,3'-ch)**, 2-pyridyl-4'-pyridyl chalcone **(2,4'-ch)**, 3-pyridyl-3'-pyridyl chalcone **(3,3'-ch)**, and 4-pyridyl-3'-pyridyl chalcone **(4,3'-ch)**,[10] 3-thienyl-2'-pyridyl chalcone **(3S,2N'-ch)**, 3-thienyl-3'-pyridyl chalcone **(3S,3N'-ch)**, 3-thienyl-phenyl chalcone **(3S,Ph'-ch)**, 3-thienyl-2'-thienyl chalcone **(3S,2S'-ch)**, and 3-thienyl-3'-thienyl chalcone **(3S,3S'-ch)**,[11] phenyl-3-thienyl chalcone **(Ph,3S'-ch)**,[12] 3-hydroxyphenyl-2'-pyridyl chalcone **(3OH,2N'-ch)**,[13] 3-hydroxyphenyl-4'-pyridyl chalcone **(3OH,4N'-ch)**,[14] phenyl-biphenyl chalcone **(Ph,BiPh'-ch)**,[15] biphenyl-phenyl chalcone **(BiPh,Ph'-ch)**, **(BiPh,BiPh'-ch)**,[16] phenyl-styryl chalcone **(Ph,Sty'-ch)**,[17] 2-pyridyl-styryl chalcone **(2N,Sty'-ch)**,[18] 3-pyridyl-styryl chalcone **(3N,Sty'-ch)**,[19] phenyl-4'-bromophenyl chalcone **(Ph,4Br'-ch)**, **(Ph,4F'-ch)**,[20] phenyl-4'-fluorophenyl chalcone **(2N,4F'-ch)**,[21] pyridazyl-3'-pyridyl **(2,5,3'-ch)**,[22] phenylpyridine bispyridinium salt **(PhSpPy-salt)**,[5d] pyridine bispyridinium salt **(SpPy-salt)**, phenylene bispyridinium salt **(Ph-BBC-salt)**,[4] phenylpyrimidine bispyridinium salt **(BTP-salt)**.[5a]

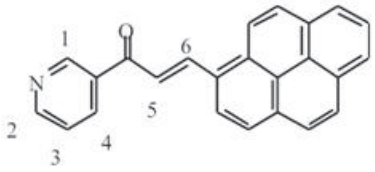
The NMR data were obtained on a Bruker DRX 400 and DRX 500 spectrometer, respectively, calibrated against the solvent signal ($CDCl_3$: ^{1}H NMR: δ = 7.27; ^{13}C NMR: δ = 77.0; DMSO-d_6: ^{1}H NMR: δ = 2.50; tetrachloroethane-d_2: ^{1}H NMR: δ = 6.00; ^{13}C NMR: δ = 74.2) and are given in ppm.

Mass specrometry was performed on a Finnigan Mat SSQ 7000 (CI) and a Bruker Reflex III (MALDI-TOF), respectively. Elemental analyses were measured on an Elementar Vario EL.

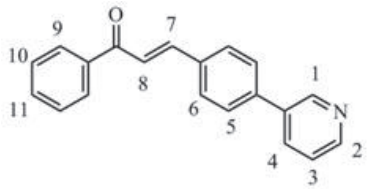
Synthesis



3-Thienyl-styryl' chalcone. To 3-acetylthiophene (**3acth**) (1.45 g, 12.0 mmol) in MeOH (30 mL) cinnamone aldehyde (**cinal**) (1.57 g, 11.9 mmol) and 2M KOH (5.0 mL) were given and refluxed for 1 d. After cooling to r.t. and the addition of aqua destillata (12 mL) a solid was filtered, washed with MeOH and dried under vacuum. Yield 21.0% (603 mg, 2.50 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (1H, dd, ^4J = 3.2 Hz, ^4J = 1.2 Hz, H^1), 7.65 (1H, dd, ^3J = 5.2 Hz, ^4J = 1.2 Hz, H^2), 7.62 (1H, dt, ^3J = 14.8 Hz, ^3J = 5.2 Hz, H^3), 7.53-7.50 (2H, m, H^8 and H^{12}), 7.41-7.36 (1H, m, H^{10}), 7.39 (1H, d, ^3J = 14.8 Hz, H^4 or H^5), 7.37 (1H, d, ^3J = 16.0 Hz, H^6 or H^7), 7.36 (1H, d, ^3J = 16.0 Hz, H^6 or H^7), 7.04-7.01 (2H, m, H^9 and H^{11}), 6.99 (1H, d, ^3J = 14.8 Hz, H^4 or H^5). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 184.0, 144.1, 143.1, 141.8, 136.1, 131.7, 129.2, 128.8, 127.4, 127.2, 126.8, 126.4, 126.1. MS (CI): calculated *m/z* for $C_{15}H_{12}OS$: 241.28 $[M+H]^+$, found: 240.90. Elemental analysis: calculated: %C 74.97, %H 5.03; found: %C 75.24, %H 4.72.

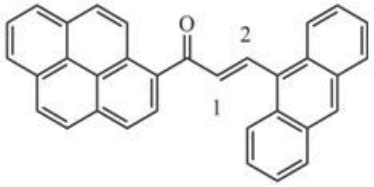


3-Pyridyl-pyrene-1-yl' chalcone. 3-Acetylpyridine (**3acpy**) (265 mg, 2.19 mmol) and pyrene-1-carbaldehyde (**P1al**) (513 mg, 2.22 mmol) in MeOH (35 mL) and 1M NaOH (5 mL) were refluxed for 24 h. The resulting precipitate was filtered and washed with MeOH. Yield: 28.4% (208 mg, 0.623 mmol). ^{1}H NMR (400 MHz, TCE-d_2): δ = 9.34 (1H, d, ^4J = 2.0 Hz, H^1), 9.02 (1H, d, ^3J = 15.2 Hz, H^5 or H^6), 8.85 (1H, d, ^3J = 4.8 Hz, H^2), 8.55 (1H, d, ^3J = 9.2 Hz, H^{pyrene}), 8.46 (1H, d, ^3J = 8.0 Hz, H^{pyrene}), 8.40 (1H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H^4), 8.30-8.27 (2H, m, H^{pyrene}), 8.24 (1H, d, ^3J = 9.2 Hz, H^{pyrene}), 8.23 (1H, d, ^3J = 8.4 Hz, H^{pyrene}), 8.19 (1H, d, ^3J = 9.2 Hz, H^{pyrene}), 8.12 (1H, d, ^3J = 8.8 Hz, H^{pyrene}), 8.09 (1H, t, ^3J = 7.6 Hz, H^{pyrene}), 7.78 (1H, d, ^3J = 15.6 Hz, H^5 or H^6), 7.53 (1H, dd, ^3J = 4.8 Hz, ^3J = 8.0 Hz, H^3). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MS (CI): calculated *m/z* for $C_{24}H_{15}NO$: 334.38 $[M+H]^+$, found: 334.12. Elemental analysis: calculated: %C 86.46, %H 4.54, %N 4.20; found: %C 86.42, %H 4.58, %N 4.36.

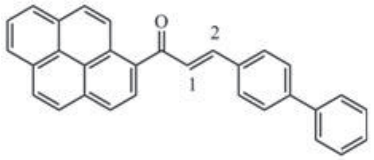


Phenylene-4-(pyrid-3-yl)' chalcone. Acetophenone (**ac**) (68.0 mg, 0.566 mmol), 4-(pyrid-3-yl)benzaldehyde (**4(3py)bal**) (103 mg, 0.562 mmol) in MeOH (18 mL) and 2 M NaOH (3 mL)

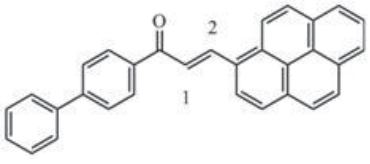
were stirred at r.t. for 2 d. The resulting solid was filtered, washed with MeOH and dried under vacuum. Yield: 37.4% (60.0 mg, 0.210 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (1H, d, ^4J = 2.0 Hz, H^1), 8.63 (1H, dd, ^4J = 1.6 Hz, ^3J = 4.8 Hz, H^4), 8.07-8.04 (2H, m, ^3J = 8.4 Hz, H^5), 7.92 (1H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H^2), 7.86 (1H, d, ^3J = 15.6 Hz, H^7 or H^8), 7.77 (2H, d, ^3J = 8.0 Hz, H^9), 7.66 (2H, d, ^3J = 8.4 Hz, H^6), 7.63-7.58 (1H, m, H^{11}), 7.60 (1H, d, ^3J = 15.6 Hz, H^7 or H^8), 7.53 (2H, t, ^3J = 8.0 Hz, H^{10}), 7.40 (1H, dd, ^3J = 4.8 Hz, ^3J = 8.0 Hz, H^3). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 190.3, 149.0, 148.2, 143.9, 139.8, 138.0, 135.6, 134.6, 134.2, 132.9, 129.2, 128.6, 128.5, 127.6, 123.6, 122.4. MS (CI): calculated *m/z* for $C_{20}H_{15}NO$: 286.34 $[M+H]^+$, found: 286.22. Elemental analysis: calculated: %C 84.19, %H 5.30, %N 4.91; found: %C 84.37, %H 5.20, %N 4.72.



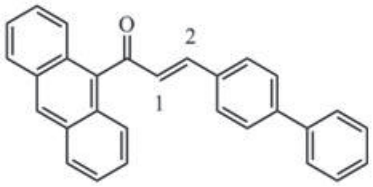
Pyrene-1-yl-anthracen-9-yl' chalcone. The synthesis was carried out according to 3-pyridyl-pyrene-1-yl chalcone (**3py-P1-ch**) with 1-acetylpyrene (**1acP**) (528 mg, 2.16 mmol), 9-anthraldehyde (**9antal**) (498 mg, 2.41 mmol), MeOH (25 mL) and 1M NaOH (5 mL). Yield: 89.8% (839 mg, 1.94 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (1H, d, ^3J = 9.2 Hz, $H^{aromat.}$), 8.68 (1H, d, ^3J = 16.0 Hz, H^1 or H^2), 8.46 (1H, s, $H^{aromat.}$), 8.41 (1H, d, ^3J = 8.0 Hz, $H^{aromat.}$), 8.33 (2H, d, ^3J = 8.0 Hz, $H^{aromat.}$), 8.29-8.21 (4H, m, $H^{aromat.}$), 8.21 (1H, d, ^3J = 8.8 Hz, $H^{aromat.}$), 8.10-8.07 (2H, m, $H^{aromat.}$), 8.02 (2H, d, ^3J = 8.0 Hz, $H^{aromat.}$), 7.55-7.48 (4H, m, $H^{aromat.}$), 7.52 (1H, d, ^3J = 16.0 Hz, H^1 or H^2). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 194.9, 142.9, 135.9, 135.5, 133.1, 131.2, 131.1, 130.6, 129.7, 129.6, 129.5, 129.4, 129.3, 128.9, 128.6, 127.1, 126.6, 126.5, 126.4, 126.2, 126.0, 125.4, 125.2, 124.9, 124.8, 124.3, 124.1. MS (CI): calculated *m/z* for $C_{33}H_{20}O$: 433.50 $[M+H]^+$, found: 433.09. Elemental analysis: calculated: %C 91.64, %H 4.66; found: %C 91.92, %H 4.51.



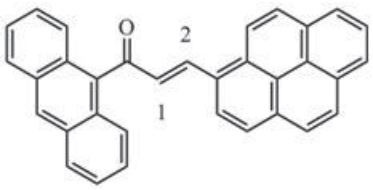
Pyren-1-yl-4-biphenyl' chalcone. The synthesis was carried out according to **3py-P1-ch** with 1-acetylpyrene (**1acP**) (500 mg, 2.05 mmol), 4-biphenyl carboxaldehyde (**4BiPhal**) (381 mg, 2.09 mol), MeOH (25 mL) and 1M NaOH (5 mL). Yield: 92.0% (770 mg, 1.88 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (1H, d, ^3J = 9.2 Hz, $H^{aromat.}$), 8.30-8.24 (4H, m, $H^{aromat.}$), 8.21 (2H, d, ^3J = 9.2 Hz, $H^{aromat.}$), 8.14 (1H, d, ^3J = 8.8 Hz, $H^{aromat.}$), 8.09 (1H, t, ^3J = 8.0 Hz, $H^{aromat.}$), 7.70 (1H, d, ^3J = 16.0 Hz, H^1 or H^2), 7.72-7.62 (6H, m, $H^{aromat.}$), 7.52 (1H, d, ^3J = 16.0 Hz, H^1 or H^2), 7.50-7.45 (2H, m, $H^{aromat.}$), 7.42-7.37 (1H, m, $H^{aromat.}$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 195.8, 145.5, 143.3, 139.9, 133.8, 133.5, 133.2, 131.0, 130.6, 129.3, 129.1, 129.04, 128.96, 128.9, 127.9, 127.5, 127.2, 127.1, 127.0, 126.3, 126.2, 126.0, 125.9, 124.8, 124.7, 124.3, 124.0. MS (CI): calculated *m/z* for $C_{31}H_{20}O$: 409.48 $[M+H]^+$, found: 409.22. Elemental analysis: calculated: %C 91.15, %H 4.93; found: %C 91.07, %H 5.03.



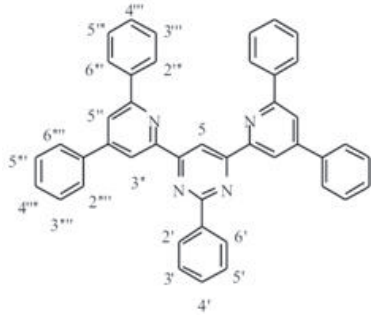
4-Biphenyl-pyrene-1-yl' chalcone. The synthesis was carried out according to **3py-P1-ch** with pyrene-1-carbaldehyde (**P1al**) (1.20 g, 5.23 mmol), 4-acetylbiphenyl (**4acBiPh**) (1.00 g, 5.10 mmol), MeOH (25 mL) and 1M NaOH (5 mL).Yield: 94.0% (1.96 g, 4.79 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.07 (1H, d, ^3J = 15.6 Hz, H^1 or H^2), 8.60 (1H, d, ^3J = 9.2 Hz, $H^{aromat.}$), 8.48 (1H, d, ^3J = 8.4 Hz, $H^{aromat.}$), 8.27-8.21 (6H, m, $H^{aromat.}$), 8.16 (1H, d, ^3J = 9.2 Hz, $H^{aromat.}$), 8.10 (1H, d, ^3J = 8.8 Hz, $H^{aromat.}$), 8.06 (1H, t, ^3J = 7.6 Hz, $H^{aromat.}$), 7.89 (1H, d, ^3J = 15.6 Hz, H^1 or H^2), 7.81-7.78 (2H, m, $H^{aromat.}$), 7.72-7.69 (2H, m, $H^{aromat.}$), 7.54-7.49 (2H, m, $H^{aromat.}$), 7.46-7.41 (1H, m, $H^{aromat.}$). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 189.6, 145.5, 141.3, 139.9, 137.0, 132.9, 131.2, 130.7, 130.3, 129.2, 128.9, 128.70, 128.69, 128.67, 128.2, 127.31, 127.28, 126.3, 126.0, 125.9, 125.0, 124.9, 124.5, 124.2, 123.8, 122.6. MS (CI): calculated *m/z* for $C_{31}H_{20}O$: 409.48 $[M+H]^+$, found: 409.19. Elemental analysis: calculated: %C 91.15, %H 4.93; found: %C 91.24, %H 4.96.



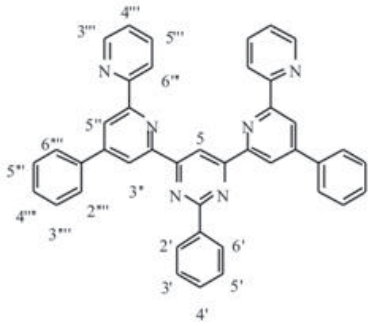
Anthracen-9-yl-4-biphenyl' chalcone. The synthesis was carried out according to **3py-P1-ch** with 4-biphenyl carboxaldehyde (**4BiPhal**) (419 mg, 2.30 mmol), 9-acetylanthracene (**9acant**) (503 mg, 2.28 mmol), MeOH (25 mL) and 1M NaOH (5 mL). Yield: 96.1% (844 mg, 2.20 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (1H, s, $H^{aromat.}$), 8.10-8.07 (2H, m, $H^{aromat.}$), 7.97-7.94 (2H, m, $H^{aromat.}$), 7.60-7.57 (4H, m, $H^{aromat.}$), 7.54-7.49 (6H, m, $H^{aromat.}$), 7.48-7.43 (2H, m, $H^{aromat.}$), 7.39-7.35 (1H, m, $H^{aromat.}$), 7.36 (1H, d, ^3J = 15.6 Hz, H^1 or H^2), 7.28 (1H, d, ^3J = 15.6 Hz, H^1 or H^2). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 200.2, 147.5, 143.7, 139.9, 134.5, 133.1, 131.1 129.2, 128.93, 128.90, 128.6, 128.4, 128.0, 127.5, 127.0, 126.6, 125.5, 125.3. MS (CI): calculated *m/z* for $C_{29}H_{20}O$: 385.46 $[M+H]^+$, found: 385.12. Elemental analysis: calculated: %C 90.60, %H 5.24; found: %C 90.44, %H 5.27.



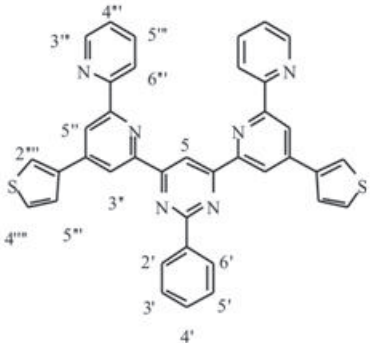
Anthracen-9-yl-pyrene-1-yl' chalcone. The synthesis was carried out according to **3py-P1-ch** with **P1al** (534 mg, 2.32 mmol), **9acant** (499 mg, 2.27 mmol), MeOH (25 mL) and 1M NaOH (5 mL). Yield: 93.4% (916 mg, 2.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (1H, s, $H^{aromat.}$), 8.49 (1H, d, ^3J = 15.6 Hz, H^1 or H^2), 8.28 (1H, d, ^3J = 8.0 Hz, $H^{aromat.}$), 8.16-8.04 (8H, m, $H^{aromat.}$), 7.97-7.95 (1H, m, $H^{aromat.}$), 7.96 (1H, d, ^3J = 15.6 Hz, H^1 or H^2), 7.87 (1H, d, ^3J = 9.6 Hz, $H^{aromat.}$), 7.81 (1H, d, ^3J = 9.2 Hz, $H^{aromat.}$), 7.58-7.51 (5H, m, $H^{aromat.}$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 199.7, 144.2, 134.9, 133.1, 131.2, 131.1, 130.6, 130.4, 130.1, 128.9, 128.74, 128.65, 128.61, 128.5, 127.8, 127.2, 126.7, 126.2, 126.1, 125.9, 125.6, 125.4, 125.0, 124.7, 124.3, 121.9. MS (CI): calculated *m/z* for $C_{33}H_{20}O$: 433.50 $[M+H]^+$, found: 433.14. Elemental analysis: calculated: %C 91.64, %H 4.66; found: %C 91.60, %H 4.67.



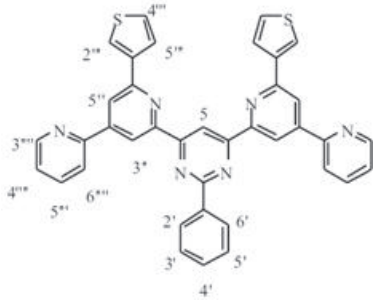
Ph,Ph'-BTP. NH_4OAc (1.20 g, 15.6 mmol), chalcone **ch** (139 mg, 0.668 mmol), and phenylpyrimidine bispyridinium iodine salt (**BTP-salt**) (203 mg, 0.312 mmol) were suspended in MeOH (5 mL) and refluxed for 24 h. A solid was filtered and dried under vacuum. Yield: 24% (47 mg, 0.076 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.87 (1H, s, H^5), 8.95 (2H, d, ^4J = 1.5 Hz, H$^{3''}$ or H$^{5''}$), 8.84-8.82 (2H, m, H$^{2'}$ and H$^{6'}$), 8.45-8.43 (4H, m, H$^{2'''}$ and H$^{6'''}$), 8.17 (2H, d, ^4J = 1.5 Hz, H$^{3''}$ or H$^{5''}$), 7.93 (4H, m, H^{Phenyl}), 7.66-7.62 (11H, m, H^{Phenyl}), 7.59-7.56 (4H, m, H^{Phenyl}). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): δ = 164.8, 157.6, 155.3, 150.9, 139.4, 139.1, 138.6, 130.8, 129.6, 129.41, 129.38, 129.0,128.88, 128.81, 128.7, 127.5, 127.4, 119.8, 118.5, 112. MALDI-TOF: calculated *m/z* for $C_{44}H_{30}N_4$: 615.70 [M+H]$^+$, found: 616.05. Elemental analysis: calculated: %C 85.97, %H 4.92, %N 9.11; found: %C 86.11, %H 4.91, %N 9.03.



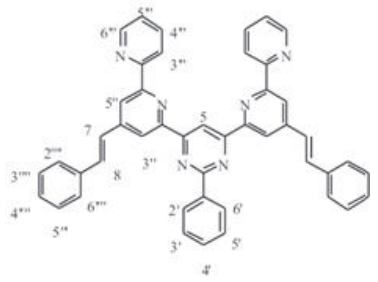
2,Ph'-BTP. The synthesis was carried out according to **Ph**,**Ph'-BTP** with NH_4OAc (1.13 g, 14.7 mmol), chalcone **2N**,**Ph'-ch** (135 mg, 0.646 mmol) and **BTP-salt** (200 mg, 0.308 mmol), MeOH (5.0 mL). Yield: 18% (36 mg, 0.058 mmol). ^{1}H NMR (500 MHz, 100°C, TCE-d_2): δ = 9.81 (1H, s, H^5), 9.04 (2H, d, ^4J = 2.0 Hz, H$^{3''}$ or H$^{5''}$), 8.95 (2H, d, ^4J = 1.5 Hz, H$^{3''}$ or H$^{5''}$), 8.92 (2H, d, ^3J = 7.5 Hz, H$^{6''}$), 8.84-8.82 (4H, m, H$^{2''}$, H$^{6''}$ and H$^{3'''}$), 8.00-7.97 (4H, m, H^{Phenyl}), 7.95 (2H, dd, ^4J = 2.0 Hz, ^3J = 7.5 Hz, H^{Phenyl}), 7.65-7.61 (7H, m, H$^{4'}$, H$^{5'''}$ and H^{Phenyl}), 7.59-7.55 (2H, m, H^{Phenyl}), 7.46-7.43 (2H, ddd, ^4J = 1.0 Hz, ^3J = 5.0, ^3J = 5.0 Hz, H$^{4'''}$). ^{13}C NMR (500 MHz, 100°C, TCE-d_2): δ = 164.5, 164.4, 156.4, 156.1, 154.5, 150.9, 149.6, 138.6, 138.1, 137.1, 131.2, 129.7, 129.5, 129.0, 128.9, 127.7, 124.5, 121.7, 120.9, 120.9, 112.3. MALDI-TOF: calculated *m/z* for $C_{42}H_{28}N_6$: 617.73 [M+H]$^+$, found: 618.08. Elemental analysis: calculated: %C 81.52, %H 4.62, %N 13.65; found: %C 81.80, %H 4.58, %N 13.63.



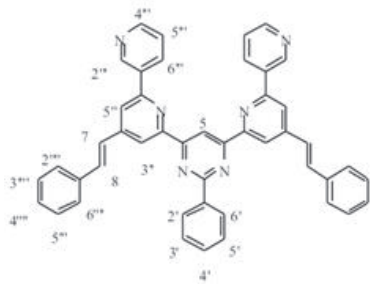
2N,3S'-BTP. The synthesis was carried out according to **Ph**,**Ph'-BTP** with chalcone **3S**,**2N'-ch** (217 mg, 1.01 mmol), **BTP-salt** (300 mg, 0.461 mmol), NH_4OAc (623 mg, 8.09 mmol) and MeOH. Yield 14.8% (43 mg, 0.0684 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.76 (1H, s, H^5), 8.98 (2H, d, ^4J = 1.5 Hz, H$^{3''}$ or H$^{5''}$), 8.89 (2H, d, ^4J = 1.5 Hz, H$^{3''}$ or H$^{5''}$), 8.87 (2H, d, ^4J = 0.5 Hz, ^4J = 1.0 Hz, ^3J = 7.5 Hz, H$^{6'''}$), 8.84-8.83 (2H, m, (H$^{2'}$ and H$^{6'}$) or (H$^{4'''}$ and H$^{6'''}$)), 8.83-8.81 (2H, m, (H$^{2'}$ and H$^{6'}$) or (H$^{4'''}$ and H$^{6'''}$)), 8.01 (2H, dd, ^4J = 1.0 Hz, ^4J = 3.0 Hz, H$^{2''''}$), 7.94 (2H, dt, ^4J = 1.5 Hz, ^3J = 7.5 Hz, H$^{4''''}$), 7.78 (2H, d, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{5''''}$), 7.68-7.62 (3H, m, H$^{3'}$, H$^{4'}$ and H$^{5'}$), 7.58 (2H, dd, ^4J = 2.5 Hz, ^3J = 5.0 Hz, H$^{4''''}$), 7.44 (2H, ddd, ^4J = 1.0 Hz, ^4J = 1.5 Hz, ^3J = 7.5 Hz, H$^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{38}H_{24}N_6S_2$: 630.59 [M+2H]$^+$, found: 630.95. Elemental analysis: calculated: %C 72.59, %H 3.85, %N 13.37; found: %C 72.30, %H 3.88, %N 13.58.



3S,2N'-BTP. The synthesis was carried out according to **Ph**,**Ph'-BTP** with chalcone **2N**,**3S'-ch** (278 mg, 1.29 mmol), **BTP-salt** (300 mg 0.461 mmol), NH_4OAc (839 mg, 1.09 mmol) and MeOH (5mL). Yield 70.7% (205 mg, 0.326 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.76 (1H, s, H^5), 9.18 (2H, d, ^4J = 1.5 Hz, H$^{3''}$ or H$^{5''}$), 8.90 (2H, ddd, ^4J = 1.0 Hz, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{3''''}$), 8.87-8.84 (2H, m, H$^{2'}$ and H$^{6'}$), 8.54 (2H, d, ^4J = 1.5 Hz, H$^{3''}$ or H$^{5''}$), 8.30 (2H, dd, ^4J = 1.0 Hz, ^4J = 3.0 Hz, H$^{2'''}$), 8.10 (2H, dd, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{5'''}$), 8.09 (2H, d, ^3J = 8.0 Hz, H$^{5''''}$), 7.99-7.92 (2H, m, H$^{4''''}$), 7.69-7.65 (3H, m, H$^{4'}$ and H$^{6''''}$), 7.64-7.60 (2H, m, H$^{3'}$ and H$^{5'}$), 7.57 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{38}H_{24}N_6S_2$: 630.59 [M+2H]$^+$, found: 630.81. Elemental analysis: calculated: %C 72.59, %H 3.85, %N 13.37; found: %C 72.85, %H 3.92, %N 12.97.

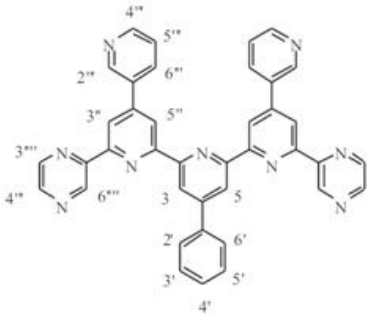


2N,Sty'-BTP. The synthesis was carried out according to **Ph**,**Ph'-BTP** with chalcone **2N**,**Sty'-ch** (329 mg, 1.40 mmol), **BTP-salt** (411mg, 0.632 mmol), NH_4OAc (1.63 g, 21.1 mmol) and MeOH (20 mL). Yield: 42.5% (180 mg, 0.269 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.73 (1H, s, H^5), 8.88-8.79 (8H, m, H$^{2'}$, H$^{6'}$, H$^{5''}$, H$^{3'''}$ and H$^{6'''}$), 7.94 (2H, td, ^4J = 1.5 Hz, ^3J = 7.5 Hz, H$^{5'''}$), 7.71-7.62 (9H, m, *i.a.* H$^{4'}$), 7.69 (2H, d, ^3J = 16.0 Hz, H^7 or H^8), 7.51-7.47 (4H, m), 7.45-7.41 (4H, m), 7.37 (2H, d, ^3J = 16.0 Hz, H^7 or H^8), the remaining unassigned peaks belong to H$^{3''}$ and H^{Phenyl}. ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{46}H_{32}N_6$: 670.84 [M+2H]$^+$, found: 670.75. Elemental analysis: calculated: %C 82.61, %H 4.82, %N 12.57; found: %C 82.81, %H 4.73, %N 12.69.

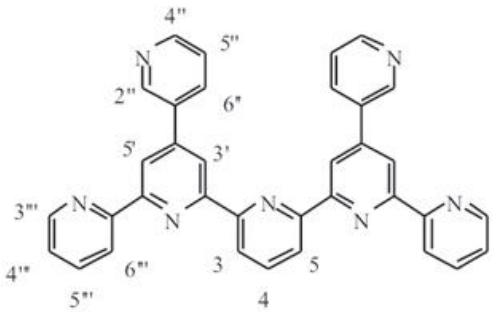


3N,Sty'-BTP. The synthesis was carried out according to **Ph**,**Ph'-BTP** with chalcone **3N**,**Sty'-ch** (146 mg, 0.621 mmol), **BTP-salt** (202 mg, 0.311 mmol), NH_4OAc (1.74 g, 22.6 mmol)

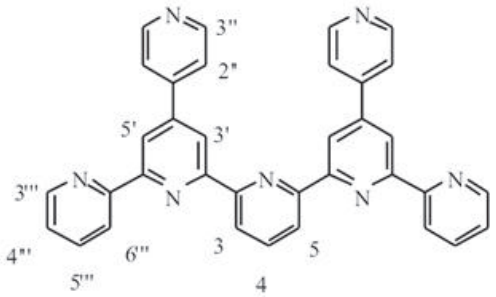
and MeOH (20 mL). Yield: 2.02% (4.20 mg, 0.00627 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.67 (1H, s, H^5), 9.52 (2H, d, ^4J = 1.0 Hz, H$^{2'''}$), 8.87-8.84 (4H, m, (H$^{2'}$ and H$^{6'}$), H$^{4'''}$ or H$^{6'''}$), 8.82-8.80 (2H, m, (H$^{2'}$ and H$^{6'}$), H$^{4'''}$ or H$^{6'''}$), 8.72-8.69 (2H, m, (H$^{2'}$ and H$^{6'}$), H$^{4'''}$ or H$^{6'''}$), 8.05 (2H, d, ^4J = 1.5 Hz, H$^{3''}$), 7.72-7.60 (11H, m), 7.62 (2H, d, ^3J = 16.5 Hz, H^7 or H^8), 7.52-7.48 (4H, m), 7.43 (2H, t, ^3J = 7.5 Hz), 7.36 (2H, d, ^3J = 16.0 Hz, H^7 or H^8), the remaining unassigned peaks belong to H$^{5''}$, H$^{5'''}$ and H^{phenyl}. ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{46}H_{32}N_6$: 521.61 [M-2C_6H_6+7H]$^+$, found: 521.83. Elemental analysis: not enough material.



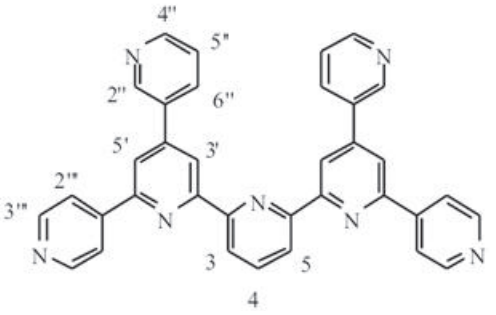
2,5,3'-PhSpPy. 2,5,3'-Azachalcone (**2,5,3'-ch**) (72.7 mg, 0.342 mmol), phenylpyridine bispyridinium iodine salt (**PhSpPy-salt**) (103 mg, 0.159 mmol) and NH_4OAc (600 mg, 7.79 mmol) were refluxed in MeOH (7 mL) for 24 h. The resulting solid was filtered, washed with MeOH and dried under vacuum. Yield 20.3% (20.0 mg, 0.0323 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 10.00 (2H, d, ^4J = 1.5 Hz, H$^{3''}$, H$^{5''}$, H$^{2'''}$ or H$^{6'''}$), 9.20 (2H, d, ^4J = 2.0 Hz, H$^{3''}$, H$^{5''}$, H$^{2'''}$ or H$^{6'''}$), 9.07 (2H, s, H^3 and H^5), 9.05 (2H, d, ^4J = 1.5 Hz, H$^{3''}$, H$^{5''}$, H$^{2'''}$ or H$^{6'''}$), 8.81 (2H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{4'''}$), 8.80 (2H, d, ^4J = 2.0 Hz, H$^{3''}$, H$^{5''}$, H$^{2'''}$ or H$^{6'''}$), 8.74 (2H, dd, ^4J = 1.5 Hz, ^4J = 2.0 Hz, H$^{3''''}$ or H$^{4'''}$), 8.71 (2H, d,^4J = 2.5 Hz, H$^{3''''}$ or H$^{4'''}$), 8.23 (2H, ddd, ^4J = 2.0 Hz, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{5'''}$), 8.04-8.02 (2H, m, (H$^{2'}$ and H$^{6'}$) or (H$^{3'}$ and H$^{5'}$)), 7.70-7.66 (2H, m, (H$^{2'}$ and H$^{6'}$) or (H$^{3'}$ and H$^{5'}$)), 7.62-7.59 (1H, m, H$^{4'}$), 7.55 (2H, ddd, ^5J = 0.5 Hz, ^3J = 5.0 Hz, ^3J = 8.0 Hz, H$^{5'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{39}H_{25}N_9$: 621.63 [M+2H]$^+$, found: 622.03. Elemental analysis: calculated: %C 75.59, %H 4.07, %N 20.34; found: %C 75.19, %H 4.13, %N 20.53.



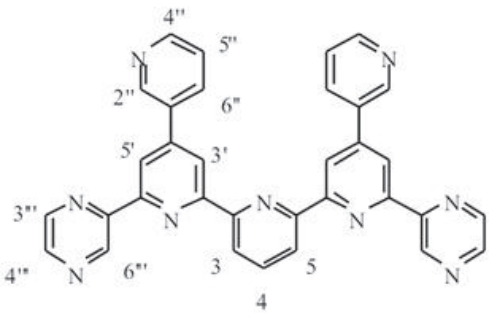
2,3'-SpPy. 2,3'-Dipyridylchalcone (**2,3'-ch**) (103 mg, 0.490 mmol), pyridine bispyridinium iodine salt (**SpPy-salt**) (140 mg, 0.244 mmol) and NH_4OAc (375 mg, 4.87 mmol) were refluxed in MeOH (7 mL) for 3 d. The filtered solid was washed with MeOH and dried under vacuum. Yield: 18.1% (24.0 mg, 0.0443 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.19 (2H, d, ^4J = 2.5 Hz, H$^{5'}$, H$^{2''}$ or H$^{6''}$), 8.95 (2H, d, ^4J = 2.0 Hz, H$^{5'}$, H$^{2''}$ or H$^{6''}$), 8.84 (2H, d, ^4J = 2.0 Hz, H$^{5'}$, H$^{2''}$ or H$^{6''}$), 8.81-8.73 (8H, m, H^3, H$^{4''}$, H$^{3'''}$ and H$^{6'''}$), 8.22 (2H, td, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{6''}$), 8.15 (1H, t, ^3J = 8.0 Hz, H^4), 7.95 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{5'''}$), 7.53 (2H, dd, ^3J = 4.5 Hz, ^3J = 7.5 Hz, H$^{5''}$), 7.42 (2H, ddd, ^4J = 1.0 Hz, ^3J = 4.5 Hz, ^3J = 7.5 Hz, H$^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{35}H_{23}N_7$: 543.58 [M+2H]$^+$, found: 543.17. Elemental analysis: calculated: %C 77.62, %H 4.28, %N 18.10; found: %C 77.58, %H 4.51, %N 17.81.



2,4'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with 2,3'-dipyridylchalcone (**2,3'-ch**) (353 mg, 1.68 mmol), **SpPy-salt** (400 mg, 0.698 mmol) and NH_4OAc (818 mg, 10.6 mmol). Yield: 52.9% (200 mg, 0.369 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.00 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.88 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.85 (4H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{3''}$), 8.81 (2H, ddd, ^4J = 1.0 Hz, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{6'''}$), 8.79 (2H, d, ^3J = 8.0 Hz, H$^{3'''}$), 8.75 (2H, td, ^4J = 1.0 Hz, ^3J = 8.0 Hz, H^3 and H^5), 8.15 (1H, t, ^3J = 7.5 Hz, H^4), 7.95 (2H, dt, ^4J = 2.0 Hz, ^3J = 7.5 Hz, H$^{5'''}$), 7.84 (4H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{2''}$), 7.43 (2H, ddd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, ^3J = 7.5 Hz, H$^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): δ = 157.1, 156.8, 156.2, 155.6, 150.9, 149.6, 147.7, 146.5, 137.0, 124.2, 122.0, 121.8, 121.6, 120.6, 119.2, 119.0. MALDI-TOF: calculated *m/z* for $C_{35}H_{23}N_7$: 543.58 [M+2H]$^+$, found: 543.40. Elemental analysis: calculated: %C 77.62, %H 4.28, %N 18.10; found: %C 77.62, %H 4.29, %N 17.94.

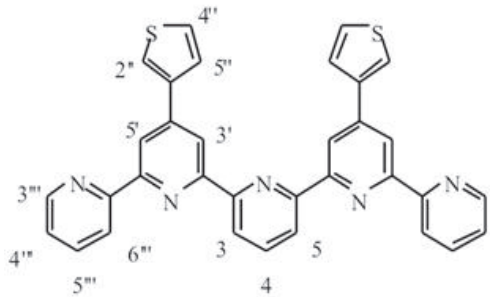


4,3'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with 4,3'-dipyridylchalcone (**4,3'-ch**) (203 mg, 0.966 mmol), **SpPy-salt** (275 mg, 0.480 mmol) and NH_4OAc (705 mg, 9.14 mmol). Yield: 32.2% (84.0 mg, 0.155 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.13 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{2''}$), 8.94 (2H, d, ^4J = 1.0 Hz, H$^{3'}$ or H$^{2''}$), 8.86 (4H, dd, ^4J = 2.0 Hz, ^3J = 4.5 Hz, H$^{3''}$), 8.81 (2H, dd, ^4J = 2.0 Hz, ^3J = 5.0 Hz, H$^{4''}$), 8.80 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.16 (4H, dd, ^4J = 2.0 Hz, ^3J = 4.5 Hz, H$^{3'''}$), 8.19-8.14 (3H, m, H^4 and H$^{6''}$), 8.09 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.55 (2H, dd, ^3J = 4.5 Hz, ^3J = 7.5 Hz, H$^{5''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{35}H_{23}N_7$: 543.58 [M+2H]$^+$, found: 543.62. Elemental analysis: calculated: %C 77.62, %H 4.28, %N 18.10; found: %C 77.73, %H 4.28, %N 17.88.

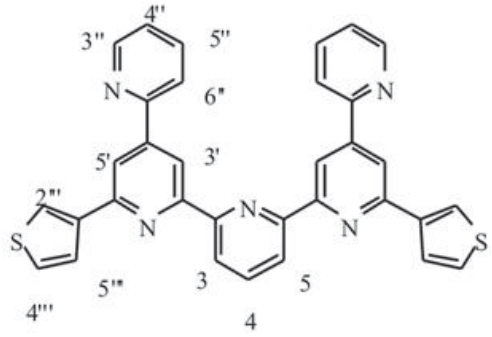


2,5,3'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **2,5,3'-ch** (253 mg, 1.20 mmol), **SpPy-salt**

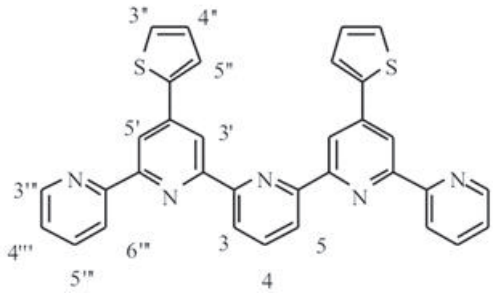
(286 mg, 0.499 mmol), NH_4OAc (2.00 g, 25.9 mmol) and MeOH (20 mL). Yield: 33.1% (90.0 mg, 0.165 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.96 (2H, d, ^4J = 1.5 Hz, H$^{3'}$, H$^{5'}$, H$^{2''}$ or H$^{6'''}$), 9.18 (2H, d, ^4J = 2.5 Hz, H$^{3'}$, H$^{5'}$, H$^{2''}$ or H$^{6'''}$), 9.00 (2H, d, ^4J = 1.5 Hz, H$^{3'}$, H$^{5'}$, H$^{2''}$ or H$^{6'''}$), 8.82-8.79 (4H, m, H^3, H$^{4''}$, H$^{3'''}$ or H$^{4'''}$), 8.77 (2H, 4J = 1.5 Hz, H$^{3'}$, H$^{5'}$, H$^{2''}$ or H$^{6'''}$), 8.74-8.70 (4H, m, H^3, H$^{4''}$, H$^{3'''}$ or H$^{4'''}$), 8.21 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{6''}$), 8.19 (1H, t, ^3J = 8.0 Hz, H^4), 7.54 (2H, ddd, ^5J = 0.5 Hz, ^3J = 5.0 Hz, ^3J = 8.0 Hz, H$^{5''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{33}H_{21}N_9$: 545.55 [M+2H]$^+$, found: 545.62. Elemental analysis: calculated: %C 72.92, %H 3.89, %N 23.19; found: %C 73.20, %H 3.72, %N 22.95.



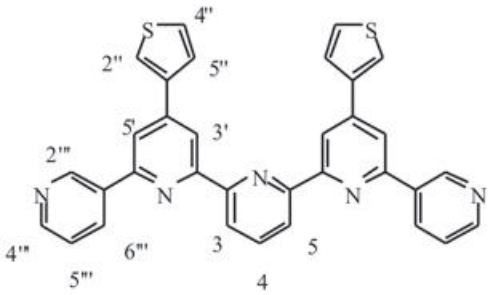
***2N,3S'-SpPy*.** The synthesis was carried out according to **2,3'-SpPy** with chalcone **2N**,**3S'-ch** (303 mg, 1.41 mmol), **SpPy-salt** (400 mg, 0.698 mmol), NH_4OAc (752 mg, 9.76 mmol) and MeOH (8 mL). Yield: 35.3% (136 mg, 0.246 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.97 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.81 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.80 (2H, ddd, ^4J = 1.0 Hz, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{3'''}$ or H$^{6'''}$), 8.75 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.73 (2H, d, ^3J = 7.5 Hz, H$^{3'''}$ or H$^{6'''}$), 8.11 (1H, t, ^3J = 8.0 Hz, H^4), 7.99 (2H, dd, ^4J = 1.0 Hz, ^4J = 3.0 Hz, H$^{2''}$), 7.94 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{5'''}$), 7.78 (2H, dd, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{5''}$), 7.58 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4''}$), 7.40 (2H, ddd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, ^3J = 7.5 Hz, H$^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{33}H_{21}N_5S_2$: 553.52 [M+2H]$^+$, found: 553.31. Elemental analysis: calculated: %C 71.84, %H 3.84, %N 12.69; found: %C 71.88, %H 3.83, %N 12.55.



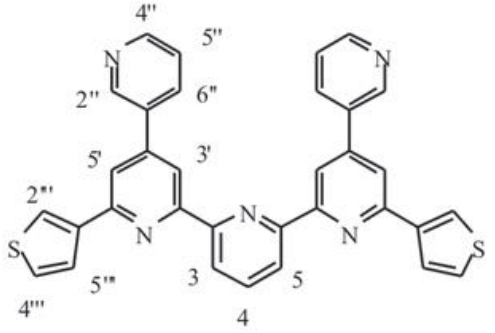
***3S,2N'-SpPy*.** The synthesis was carried out according to **2,3'-SpPy** with chalcone **3S**,**3N'-ch** (441 mg, 2.05 mmol), **SpPy-salt** (588 mg 1.03 mmol), NH_4OAc (1.61 g, 2.09 mmol) and MeOH (18 mL). Yield 35.3% (201 mg, 0.364 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.23 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.88 (2H, ddd, ^4J = 1.0 Hz, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{3''}$), 8.74 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.43 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.20 (2H, dd, ^4J = 1.0 Hz, ^4J = 3.0 Hz, H$^{2'''}$), 8.11 (1H, t, ^3J = 8.0 Hz, H^4), 8.09 (2H, d, ^3J = 8.0 Hz, H$^{6''}$), 7.99 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, H$^{5'''}$), 7.91 (2H, td, ^4J = 1.5 Hz, ^3J = 8.0 Hz, H$^{5''}$), 7.52 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4'''}$), 7.43 (2H, ddd, ^4J = 1.0 Hz, ^4J = 4.5 Hz, ^3J = 7.5 Hz, H$^{4''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{33}H_{21}N_5S_2$: 553.52 [M+2H]$^+$, found: 553.34. Elemental analysis: calculated: %C 71.84, %H 3.84, %N 12.69; found: %C 71.61, %H 3.82, %N 12.57.



***2N,2S'-SpPy*.** The synthesis was carried out according to **2,3'-SpPy** with chalcone **2N**,**2S'-ch** (210 mg, 0.976 mmol), **SpPy-salt** (240 mg, 0.419 mmol), NH_4OAc (1.20 g, 15.6 mmol) and MeOH (10 mL). Yield: 52.7% (122 mg, 0.221 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.04 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.82-8.80 (2H, m, (H^3 and H^5), H$^{3'''}$ or H$^{6'''}$), 8.81 (2H, d, ^4J = 2.0 Hz, H$^{3'}$ or H$^{5'}$), 8.75 (2H, d, ^3J = 8.0 Hz, (H^3 and H^5), H$^{3'''}$ or H$^{6'''}$), 8.73-8.71 (2H, m, (H^3 and H^5), H$^{3'''}$ or H$^{6'''}$), 8.11 (1H, t, ^3J = 7.5 Hz, H^4), 7.94 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{5'''}$), 7.87 (2H, dd, ^4J = 1.0 Hz, ^3J = 4.0 Hz, H$^{3''}$), 7.56 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, H$^{5''}$), 7.41 (2H, ddd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, ^3J = 7.5 Hz, H$^{4'''}$), 7.28 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, H$^{4''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{33}H_{21}N_5S_2$: 553.52 [M+2H]$^+$, found: 553.25. Elemental analysis: calculated: %C 71.84, %H 3.84, %N 12.69; found: %C 72.05, %H 3.74, %N 12.80.

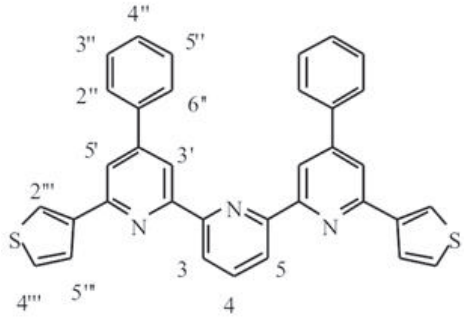


***3N,3S'-SpPy*.** The synthesis was carried out according to **2,3'-SpPy** with chalcone **3N**,**3S'-ch** (377 mg, 1.75 mmol), **SpPy-salt** (450 mg, 0.816 mmol), NH_4OAc (1.20 g, 15.6 mmol) and MeOH (10 mL). Yield: 2.66% (12.0 mg, 0.0218 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.48 (2H, dd, ^4J = 1.0 Hz, ^4J = 2.5 Hz, H$^{2'''}$), 8.93 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.76 (2H, dd, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{4'''}$), 8.74 (2H, d, ^3J = 7.5 Hz, H^3 and H^5), 8.57 (2H, ddd, ^4J = 2.0 Hz, ^4J = 2.5 Hz, ^3J = 8.0 Hz, H$^{6'''}$), 8.11 (1H, t, ^3J = 8.0 Hz, H^4), 8.04 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.93 (2H, dd, ^4J = 1.0 Hz, ^4J = 3.0 Hz, H$^{2''}$), 7.71 (2H, dd, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{5''}$), 7.60 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4''}$), 7.51 (2H, ddd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, ^3J = 8.0 Hz, H$^{5'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{33}H_{21}N_5S_2$: 553.52 [M+2H]$^+$, found: 553.03. Elemental analysis: not enough material.

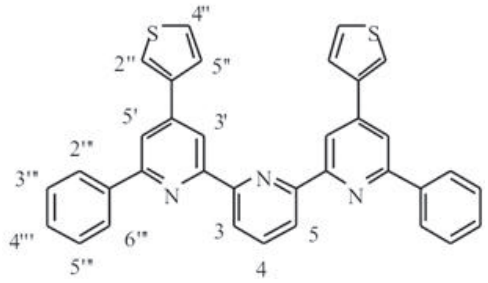


***3S,3N'-SpPy*.** The synthesis was carried out according to **2,3'-SpPy** with chalcone **3S**,**3N'-ch** (210 mg, 0.975 mmol), **SpPy-salt** (250 mg, 0.436 mmol), NH_4OAc (1.20 g, 15.6 mmol) and MeOH (10 mL). Yield: 10.3% (25.0 mg, 0.0453 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.12-9.10 (2H, m, H$^{2''}$), 8.79 (2H, d, ^4J = 1.5 Hz,

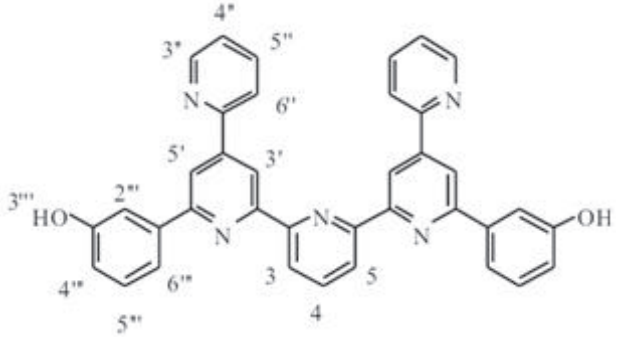
H$^{3'}$), 8.78 (2H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{4''}$), 8.75 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.17 (2H, dd, ^4J = 1.5 Hz, ^4J = 3.0 Hz, H$^{2'''}$), 8.15-8.12 (2H, m, H$^{6''}$), 8.11 (1H, t, ^3J = 8.0 Hz, H^4), 7.93 (2H, dd, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{5'''}$), 7.90 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.54-7.50 (4H, m, H$^{5''}$ and H$^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{33}H_{21}N_5S_2$: 553.52 $[M+2H]^+$, found: 553.08. Elemental analysis: calculated: %C 71.84, %H 3.84, %N 12.69; found: %C 71.92, %H 3.77, %N 12.79.



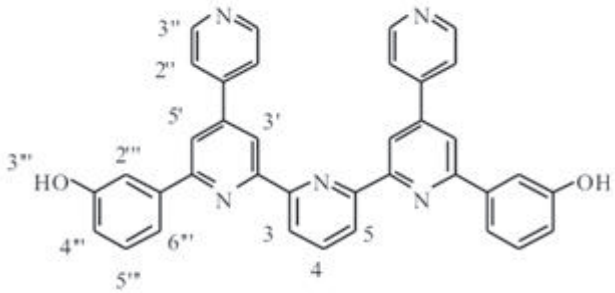
3S,Ph'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **3S,Ph'-ch** (289 mg, 1.34 mmol), **SpPy-salt** (352 mg, 0.614 mmol), NH_4OAc (1.37 g, 17.8 mmol) and MeOH (10 mL). Yield: 10.3% (35.0 mg, 0.0636 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.90 (2H, d, ^4J = 2.0 Hz, H$^{3'}$), 8.73 (2H, d, ^3J = 7.5 Hz, H^3 and H^5), 8.16 (2H, dd, ^4J = 1.5 Hz, ^4J = 3.0 Hz, H$^{2'''}$), 8.09 (1H, t, ^3J = 7.5 Hz, H^4), 7.95-7.89 (8H, m, H$^{5'}$, H$^{5'''}$ and H^{Phenyl}), 7.62-7.58 (4H, m, H^{Phenyl}), 7.56-7.54 (2H, m, H^{Phenyl}), 7.52 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{33}H_{21}N_5S_2$: 550.53 $[M+H]^+$, found: 550.47. Elemental analysis: calculated: %C 76.47, %H 4.22, %N 7.64; found: %C 76.29, %H 4.37, %N 8.00.



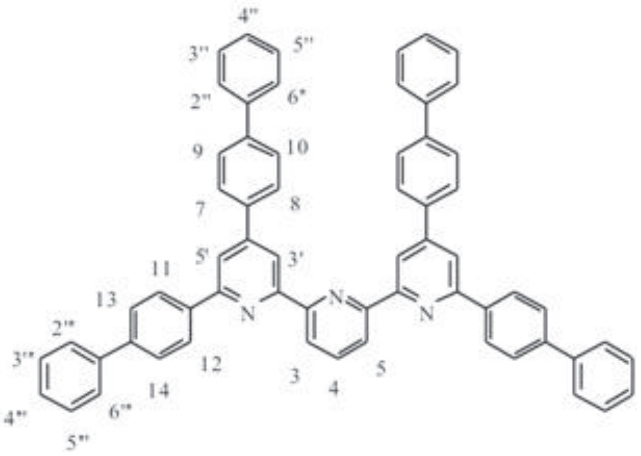
Ph,3S'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **Ph,3S'-ch** (287 mg, 1.34 mmol), **SpPy-salt** (362 mg, 0.631 mmol), NH_4OAc (1.37 g, 17.8 mmol) and MeOH (10 mL). Yield: 1.21% (4.20 mg, 0.00764 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.89 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.76 (2H, d, ^3J = 7.5 Hz, H^3 and H^5), 8.29-8.27 (4H, m, H$^{2'''}$ and H$^{6'''}$), 8.10 (1H, t, ^3J = 7.5 Hz, H^4), 8.04 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.92 (2H, dd, ^4J = 1.0 Hz, ^4J = 3.0 Hz, H$^{2''}$), 7.71 (2H, dd, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{5''}$), 7.62-7.57 (6H, m, H$^{4''}$ and H^{Phenyl}), 7.55-7.51 (2H, m, H^{Phenyl}). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{33}H_{21}N_5S_2$: 551.53 $[M+H]^+$, found: 551.27. Not enough material for an elemental analysis.



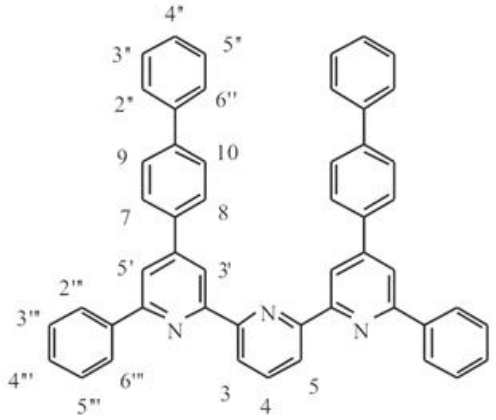
3OH,2N'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **3OH,2N'-ch** (164 mg, 0.728 mmol), **SpPy-salt** (203 mg, 0.354 mmol), NH_4OAc (732 mg, 9.50 mmol) and MeOH (10 mL). Yield: 35.0% (71.0 mg, 0.124 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.29-9-28 (2H, m, H$^{3'}$), 8.89-8.80 (2H, m, H$^{3''}$), 8.77 (2H, d, ^3J = 7.5 Hz, H^3 and H^5), 8.55-8.54 (2H, m, H$^{5'}$), 8.13-8.10 (2H, m, H$^{5''}$, H$^{2'''}$ or H$^{6'''}$), 8.11 (1H, t, ^3J = 7.5 Hz, H^4), 7.94-7.88 (6H, m, H$^{5''}$, H$^{6''}$, H$^{2'''}$ or H$^{6'''}$), 7.49-7.42 (4H, m, H$^{4''}$ and H$^{5'''}$), 7.03-7.00 (2H, m, H$^{4'''}$), 4.85 (2H, s (br), H$^{3'''}$). MALDI-TOF: calculated *m/z* for $C_{37}H_{25}N_5O_2$: 572.60 $[M+H]^+$, found: 572.67. Elemental analysis: calculated: %C 77.74, %H 4.41, %N 12.25; found: %C 77.55, %H 4.34, %N 12.36.



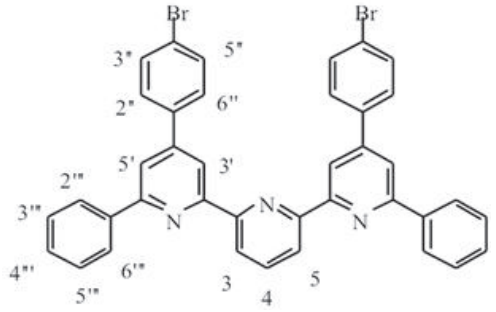
3OH,4N'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **3OH,4N'-ch** (180 mg, 0.799 mmol), **SpPy-salt** (223 mg, 0.389 mmol), NH_4OAc (814 mg, 10.6 mmol) and MeOH (10 mL). Yield: 5.4% (12.0 mg, 0.0209 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.90 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.85 (4H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{3''}$), 8.79 (2H, d, ^3J = 8.0 Hz, H^3), 8.14 (1H, t, ^3J = 8.0 Hz, H^4), 8.04 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.85-7.83 (4H, m, H$^{2'''}$ and H$^{6'''}$), 7.77 (4H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{2''}$), 7.48 (2H, t, ^3J = 8.0 Hz, H$^{5'''}$), 7.05-7.02 (2H, m, H$^{4'''}$), 4.91 (2H, s (br), H$^{3'''}$). MALDI-TOF: calculated *m/z* for $C_{37}H_{25}N_5O_2$: 573.60 $[M+2H]^+$, found: 573.44. Not enough material for an elemental analysis.



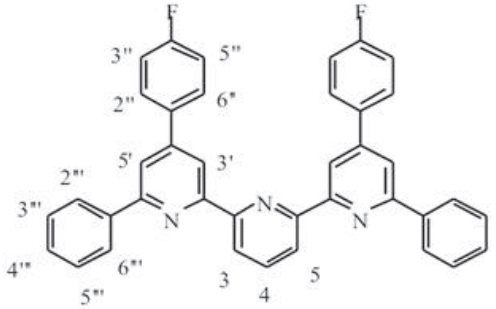
BiPh,BiPh'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **BiPh,BiPh'-ch** (186 mg, 0.516 mmol), **SpPy-salt** (150 mg, 0.261 mmol), NH_4OAc (830 mg, 10.8 mmol) and MeOH (10 mL). Yield: 57.6% (127 mg, 0.150 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.07 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.82 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.41 (4H, d, ^3J = 8.5 Hz, H^{11} and H^{12}), 8.18 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 8.15 (2H, t, ^3J = 7.5 Hz, H^4), 8.05 (4H, d, ^3J = 8.5 Hz, H^{Phenyl}), 7.88-7.85 (8H, m, H^{Phenyl}), 7.77 (4H, d, ^3J = 7.5 Hz, H^{Phenyl}), 7.73 (4H, d, ^3J = 7.5 Hz, H^{Phenyl}), 7.56-7.50 (8H, m, H^{Phenyl}), 7.47-7.42 (4H, m, H^{Phenyl}). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low; MALDI-TOF: calculated *m/z* for $C_{63}H_{43}N_3$: 842.96 $[M+2H]^+$, found: 843.28. Elemental analysis: calculated: %C 89.86, %H 5.15, %N 4.99; found: %C 89.80, %H 5.10, %N 5.07.



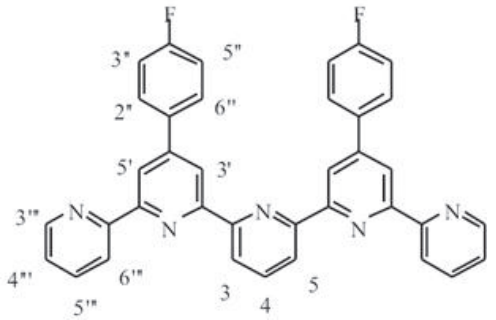
Ph,BiPh'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **Ph,BiPh'-ch** (299 mg, 1.05 mmol), **SpPy-salt** (306 mg, 0.534 mmol), NH_4OAc (1.37 g, 17.8 mmol) and MeOH (10 mL). Yield: 9.0% (33.1 mg, 0.0480 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.06 (2H, d, ^4J = 1.5 Hz, $H^{3'}$), 8.79 (2H, d, ^3J = 8.0 Hz), 8.34-8.32 (4H, m, $H^{2'''}$ and $H^{6'''}$), 8.13 (2H, d, ^4J = 1.5 Hz, $H^{5'}$), 8.12 (1H, t, ^3J = 8.0 Hz, H^4), 8.03 (4H, d, ^3J = 8.5 Hz, H^{Phenyl}), 7.86 (4H, d, ^3J = 8.0 Hz, H^{Phenyl}), 7.74-7.71 (4H, m, H^{Phenyl}), 7.64-7.60 (4H, m, H^{Phenyl}), 7.56-7.49 (6H, m, H^{Phenyl}), 7.47-7.42 (2H, m, H^{Phenyl}). MALDI-TOF: calculated *m/z* for $C_{51}H_{35}N_3$: 691.80 $[M+2H]^+$, found: 691.30. Elemental analysis: calculated: %C 88.79, %H 5.11, %N 6.09; found: %C 88.94, %H 5.22, %N 6.15.



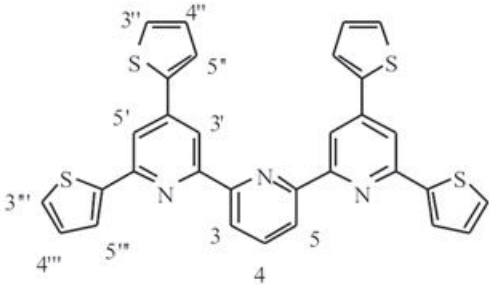
4Br'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **Ph,4Br'-ch** (301 mg, 1.05 mmol), **SpPy-salt** (305 mg, 0.532 mmol), NH_4OAc (1.37 g, 17.7 mmol) and MeOH (10 mL). Yield: 5.5% (20.4 mg, 0.0293 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.84 (2H, d, ^4J = 1.5 Hz, $H^{3'}$), 8.77 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.29-8.28 (4H, m, $H^{2'''}$ and $H^{6'''}$), 8.11 (1H, t, ^3J = 8.0 Hz, H^4), 8.02 (2H, d, ^4J = 2.0 Hz, $H^{5'}$), 7.78-7.73 (8H, m, H^{Phenyl}), 7.62-7.58 (4H, m, H^{Phenyl}), 7.55-7.51 (2H, m, $H^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{39}Br_2H_{25}N_3$: 697.03 $[M+2H]^+$, found: 696.91. Elemental analysis: calculated: %C 67.36, %H 3.62, %N 6.04; found: %C 67.20, %H 3.55, %N 6.13.



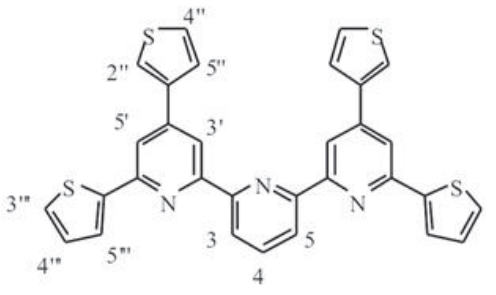
4F'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **Ph,4F'-ch** (233 mg, 1.03 mmol), **SpPy-salt** (297 mg, 0.518 mmol), NH_4OAc (1.26 g, 16.4 mmol) and MeOH (10 mL). Yield: 10.8% (32.2 mg, 0.0561 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.87 (2H, d, ^4J = 1.5 Hz, $H^{3'}$), 8.78 (2H, d, ^3J = 7.5 Hz, H^3 and H^5), 8.30-8.28 (4H, m, $H^{2'''}$ and $H^{6'''}$), 8.11 (1H, t, ^3J = 7.5 Hz, H^4), 8.02 (2H, d, ^4J = 1.5 Hz, $H^{5'}$), 7.91-7.87 (4H, m, $H^{aromat.}$), 7.62- 7.58 (4H, m, $H^{aromat.}$), 7.55-7.51 (2H, m, $H^{4'''}$), 7.32-7.27 (4H, m, $H^{aromat.}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): δ = 156.9, 155.8, 149.3, 139.7, 137.9, 135.5, 129.40, 129.38, 129.2, 129.1, 129.0, 127.4, 121.9, 120.63, 120.60, 118.4, 117.7, 116.4, 116.2. MALDI-TOF: calculated *m/z* for $C_{39}H_{25}F_2N_3$: 574.61 $[M+H]^+$, found: 574.94.



2N,4F'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **2N,4F'-ch** (378 mg, 1.66 mmol), **SpPy-salt** (421 mg, 0.735 mmol), NH_4OAc (1.47 g, 19.1 mmol) and MeOH (20 mL). Yield: 35.7% (151 mg, 0.262 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.98 (2H, d, ^4J = 1.5 Hz, $H^{3'}$ or $H^{5'}$), 8.82 (2H, d, ^4J = 1.5 Hz, $H^{3'}$ or $H^{5'}$), 8.83-8.81 (2H, m, $H^{3'''}$), 8.79 (2H, d, ^3J = 8.0 Hz, H^3 or $H^{6'}$), 8.76 (2H, d, ^3J = 8.0 Hz, H^3 or $H^{6'}$), 8.15 (1H, t, ^3J = 8.0 Hz, H^4), 8.00-7.96 (6H, m, $H^{2''}$, $H^{6''}$ and $H^{5'''}$), 7.45-7.41 (2H, m, $H^{4'''}$), 7.34-7.29 (4H, m, $H^{3''}$ and $H^{5''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{37}H_{23}F_2N_5$: 576.58 $[M+H]^+$, found: 576.94.

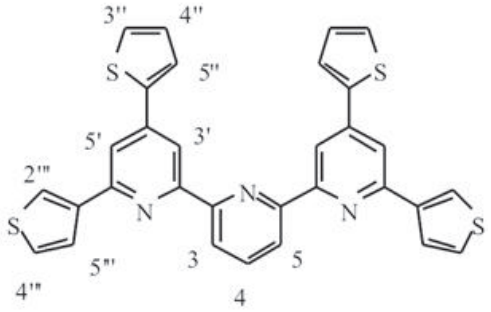


2S,2S'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **2S,2S'-ch** (452 mg, 2.05 mmol), **SpPy-salt** (587 mg, 1.02 mmol), NH_4OAc (1.95 g, 25.4 mmol) and MeOH (20 mL). Yield: 0.260% (1.50 mg, 0.00267 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.86 (2H, d, ^4J = 1.5 Hz, $H^{3'}$), 8.69 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.09 (1H, t, ^3J = 8.0 Hz, H^4), 7.92 (2H, d, ^4J = 1.5 Hz, $H^{5'}$), 7.83 (2H, dd, ^4J = 1.0 Hz, ^3J = 3.5 Hz, $H^{5'''}$), 7.77 (2H, dd, ^4J = 1.0 Hz, ^3J = 3.5 Hz, $H^{5''}$), 7.56 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, $H^{3''}$ or $H^{3'''}$), 7.51 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, $H^{3''}$ or $H^{3'''}$), 7.28 (2H, dd, ^3J = 5.0 Hz, ^3J = 5.0 Hz, $H^{4''}$), 7.24 (2H, dd, ^3J = 5.0 Hz, ^3J = 5.0 Hz, $H^{4'''}$). MALDI-TOF: calculated *m/z* for $C_{31}H_{19}N_3S_4$: 562.53 $[M+2H]^+$, found: 562.58. Not enough material for an elemental analysis.

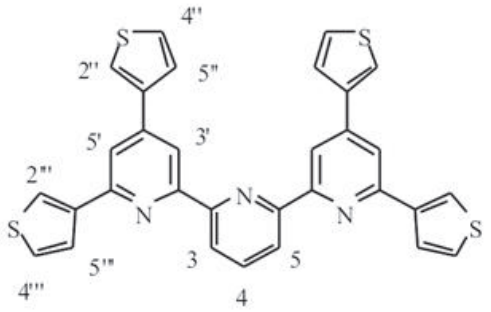


2S,3S'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **2S,3S'-ch** (407 mg, 1.85 mmol), **SpPy-salt**

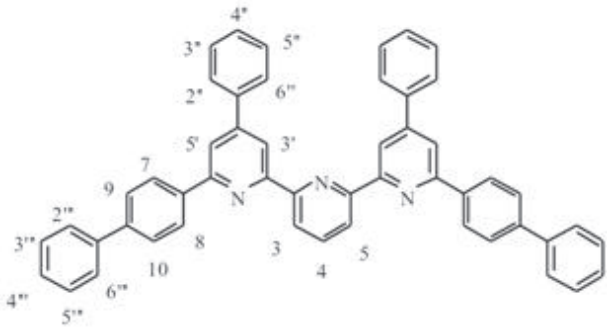
(516 mg, 0.900 mmol), NH_4OAc (1.87 g, 24.3 mmol) and MeOH (20 mL). Yield: 0.860% (4.35 mg, 0.00774 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.79 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.69 (2H, d, ^3J = 7.5 Hz, H^3 and H^5), 8.09 (1H, t, ^3J = 7.5 Hz, H^4), 7.92 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.89 (2H, dd, ^4J = 1.5 Hz, ^4J = 3.0 Hz, H$^{2''}$), 7.83 (2H, dd, ^4J = 1.0 Hz, ^3J = 3.5 Hz, H$^{5'''}$), 7.68 (2H, dd, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{5''}$), 7.58 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4''}$), 7.51 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, H$^{3'''}$), 7.23 (2H, dd, ^4J = 3.5 Hz, ^3J = 5.0 Hz, H$^{4'''}$). MALDI-TOF: calculated *m/z* for $C_{31}H_{19}N_3S_4$: 562.53 [M+H]$^+$, found: 563.02. Not enough material for an elemental analysis.



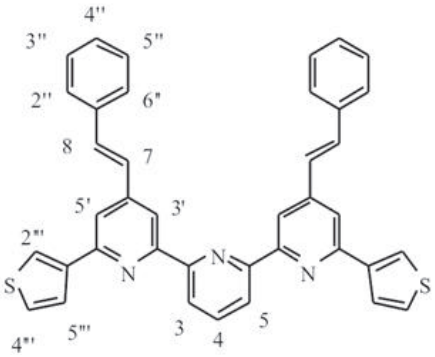
3S,2S'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **3S,2S'-ch** (440 mg, 2.00 mmol), **SpPy-salt** (502 mg,0.88 mmol), NH_4OAc (2.08 g, 27.0 mmol) and MeOH (20 mL). Yield: 13.6% (67.2 mg, 0.119 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.89 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.70 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.15 (2H, dd, ^4J = 1.0 Hz, ^4J = 3.0 Hz, H$^{2'''}$), 8.07 (1H, t, ^3J = 8.0 Hz, H^4), 7.91 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, H$^{5'''}$), 7.90 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.77 (2H, dd, ^4J = 1.0 Hz, ^3J = 3.5 Hz, H$^{5''}$), 7.55 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, H$^{3''}$ or H$^{4'''}$), 7.52 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{3''}$ or H$^{4'''}$), 7.27 (2H, dd, ^3J = 3.5 Hz, ^3J = 5.0 Hz, H$^{4''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): δ = 157.0, 155.5, 153.9, 143.4, 142.7, 142.5, 137.9, 128.6, 127.2, 126.9, 126.4, 125.6, 124.2, 121.7, 120.6, 116.7, 116.2. MALDI-TOF: calculated *m/z* for $C_{31}H_{19}N_3S_4$: 562.53 [M+H]$^+$, found: 563.14. Elemental analysis: calculated: %C 68.28, %H 3.41, %N 7.48; found: %C 68.23, %H 3.51, %N 7.42.



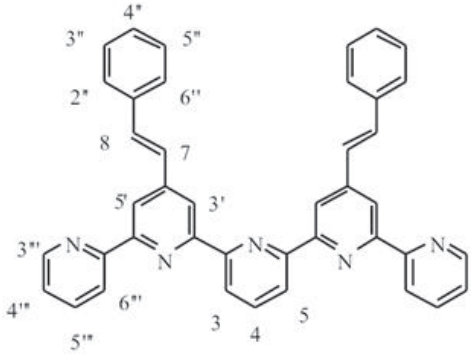
3S,3S'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **3S,3S'-ch** (618 mg, 2.81 mmol), **SpPy-salt** (804 mg, 1.40 mmol), NH_4OAc (1.68 g, 21.7 mmol) and MeOH (20 mL). Yield: 30.8% (243 mg, 0.432 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.82 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.71 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.14 (2H, dd, ^4J = 3.0 Hz, ^4J = 1.5 Hz, H$^{2'''}$), 8.08 (1H, t, ^3J = 8.0 Hz, H^4), 7.92 (2H, dd, ^4J = 3.0 Hz, ^4J = 1.0 Hz, H$^{2''}$), 7.91 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.89 (2H, dd, ^3J = 3.0 Hz, ^4J = 1.0 Hz, H$^{5'''}$), 7.69 (2H, dd, ^3J = 5.0 Hz, ^4J = 1.5 Hz, H$^{5''}$), 7.58 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4''}$ or H$^{4'''}$), 7.52 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4''}$ or H$^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): δ = 157.0, 155.8, 153.9, 144.7, 142.9, 140.7, 137.8, 127.2, 126.9, 126.4, 126.3, 124.1, 123.3, 121.7, 120.6, 117.6, 117.0. MALDI-TOF: calculated *m/z* for $C_{31}H_{19}N_3S_4$: 562.53 [M+H]$^+$, found: 563.05. Elemental analysis: calculated: %C 66.28, %H 3.41, %N 7.48; found: %C 66.39, %H 3.59, %N 7.19.



BiPh,Ph'SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **BiPh,Ph'-ch** (493 mg, 1.73 mmol), **SpPy-salt** (496 mg, 0.865 mmol), NH_4OAc (1.71 g, 22.1 mmol) and MeOH (20 mL). Yield: 7.62% (45.5 mg, 0.0659 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.98 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.82 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.41-8.38 (4H, m, H^7 and H^8), 8.134 (1H, t, ^3J = 8.0 Hz, H^4), 8.127 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.97-7.94 (4H, m, H^{Phenyl}), 7.86-7.83 (4H, m, H^{Phenyl}), 7.78-7.75 (4H, m, H^{Phenyl}), 7.64-7.60 (4H, m, H^{Phenyl}), 7.58-7.52 (6H, m, H^{Phenyl}), 7.46-7.42 (2H, m, H^{Phenyl}). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): δ = 157.1, 156.9, 155.9, 150.3, 142.1, 140.9, 139.3, 138.8, 137.9, 129.4, 129.3, 129.0, 127.8, 127.7, 127.4, 127.3, 121.8, 120.6, 118.4, 118.0. MALDI-TOF: calculated *m/z* for $C_{51}H_{35}N_3$: 690.79 [M+H]$^+$, found: 691.17. Elemental analysis: calculated: %C 88.79, %H 5.11, %N 6.09; found: %C 88.61, %H 5.15, %N 6.20

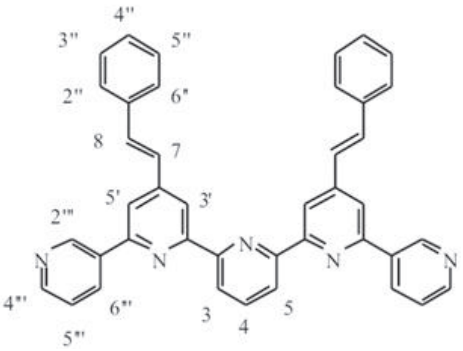


3S,Sty'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **3S,Sty'-ch** (494 mg, 2.01 mmol), **SpPy-salt** (588 mg,1.03 mmol), NH_4OAc (1.63 g, 21.1 mmol) and MeOH (20 mL). Yield: 0.874 % (5.40 mg, 0.00897 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.77 (2H, d, ^4J = 1.0 Hz, H$^{3'}$), 8.70 (2H, d, ^3J = 8.0 Hz, H^3 and H^5), 8.14 (2H, dd, ^4J = 1.0 Hz, ^4J = 3.0 Hz, H$^{2'''}$), 8.07 (1H, t, ^3J = 7.5 Hz, H^4), 7.92 (2H, dd, ^4J = 1.5 Hz, ^3J = 5.0 Hz, H$^{5'''}$), 7.79 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 7.66 (4H, d, ^3J = 7.5 Hz, H$^{2''}$ and H$^{6''}$), 7.59 (2H, d, ^3J = 16.0 Hz, H^7 or H^8), 7.52 (2H, dd, ^4J = 3.0 Hz, ^3J = 5.0 Hz, H$^{4'''}$), 7.44 (4H, t, ^3J = 7.5 Hz, H$^{3''}$ and H$^{5''}$), 7.41-7.39 (2H, m, H$^{4''}$), 7.32 (2H, d, ^3J = 16.0 Hz, H^7 or H^8). MALDI-TOF: calculated *m/z* for $C_{39}H_{27}N_3S_2$: 603.59 [M+2H]$^+$, found: 603.29. Not enough material for an elemental analysis.

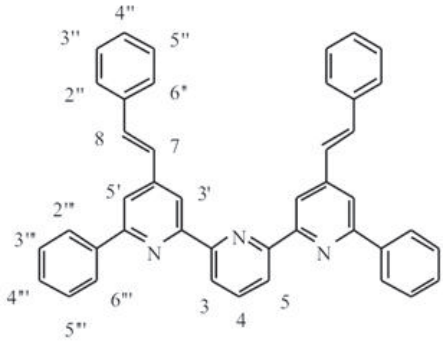


2N,Sty'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **2N,Sty'-ch** (468 mg, 1.99 mmol), **SpPy-salt**

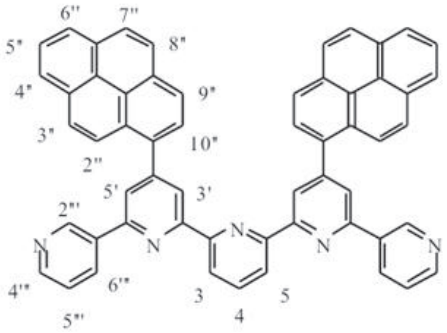
(570 mg, 0.994 mmol), NH_4OAc (1.96 g, 25.4 mmol) and MeOH (20 mL). Yield: 28.0% (165 mg, 0.278 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.89 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.82-8.81 (2H, m, H$^{3'''}$), 8.75 (2H, d, ^3J = 8.0 Hz, (H^3 and H^5) or H$^{6'''}$), 8.72 (2H, d, ^3J = 8.0 Hz, (H^3 and H^5) or H$^{6'''}$), 8.69 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 8.11 (1H, t, ^3J = 8.0 Hz, H^4), 7.93 (2H, td, ^3J = 8.0 Hz, ^4J = 2.0 Hz, H$^{5'''}$), 7.70-7.66 (4H, m, H$^{2''}$ and H$^{6''}$), 7.68 (2H, d, ^3J = 16.0 Hz, H^7 or H^8), 7.47-7.43 (4H, m, H$^{3''}$ and H$^{5''}$), 7.42-7.40 (4H, m, H$^{4''}$ and H$^{4'''}$), 7.40 (2H, d, ^3J = 16.0 Hz, H^7 or H^8). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{41}H_{29}N_5$: 592.67 $[M+H]^+$, found: 593.08. Elemental analysis: calculated: %C 83.22, %H 4.94, %N 11.84; found: %C 83.12, %H 4.80, %N 12.01



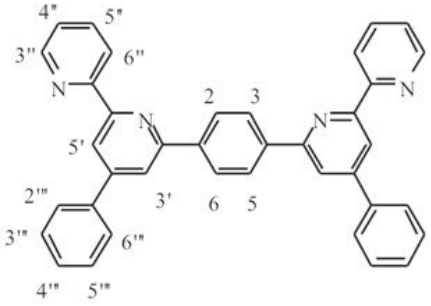
3N,Sty'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **3N**,**Sty'-ch** (438 mg, 1.86 mmol), **SpPy-salt** (536 mg, 0.935 mmol), NH_4OAc (1.70 g, 22.1 mmol) and MeOH (20 mL). Yield: 6.86% (38.0 mg, 0.0642 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.48-9.47 (2H, m, H$^{2'''}$), 8.87 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 8.76 (2H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{6''}$), 8.74 (2H, d, ^3J = 7.5 Hz, H^3 and H^5), 8.57 (2H, td, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{4'''}$), 8.10 (1H, t, ^3J = 8.0 Hz, H^4), 7.93 (2H, d, ^4J = 1.0 Hz, H$^{5'}$), 7.67-7.66 (4H, m, H$^{2''}$ and H$^{6''}$), 7.62 (2H, d, ^3J = 16.0 Hz, H^7 or H^8), 7.52 (2H, dd, ^3J = 4.5 Hz, ^3J = 8.0 Hz, H$^{5'''}$), 7.47-7.39 (6H, m, H$^{3''}$, H$^{4''}$ and H$^{5''}$), 7.35 (2H, d, ^3J = 16.0 Hz, H^7 or H^8). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low; MALDI-TOF: calculated *m/z* for $C_{41}H_{29}N_5$: 593.67 $[M+2H]^+$, found: 593.41. Elemental analysis: calculated: %C 83.22, %H 4.94, %N 11.84; found: %C 83.08, %H 4.76, %N 12.09



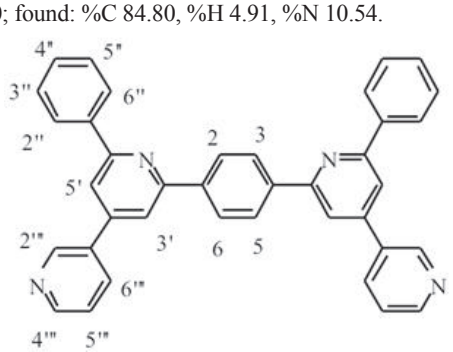
Ph,Sty'-SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **Ph**,**Sty'-ch** (457 mg, 1.95 mmol), **SpPy-salt** (559 mg, 0.975 mmol), NH_4OAc (1.76 g, 22.8 mmol) and MeOH (20 mL). Yield: 4.69% (27.0 mg, 0.0457 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.83 (2H, d, ^4J = 1.0 Hz, H$^{3'}$), 8.76 (2H, d, ^3J = 7.5 Hz, H^3 and H^5), 8.29-8.27 (4H, m, H$^{2'''}$ and H$^{6'''}$), 8.09 (1H, t, ^3J = 8.0 Hz, H^4), 7.93 (2H, t, ^4J = 1.0 Hz, H$^{5'}$), 7.68-7.66 (4H, m, H^{Phenyl}), 7.62-7.58 (4H, m, H^{Phenyl}), 7.61 (2H, d, ^3J = 16.0 Hz, H^7 or H^8), 7.54-7.52 (2H, m, H^{Phenyl}), 7.47-7.43 (4H, m, H^{Phenyl}), 7.41-7.39 (2H, m, H^{Phenyl}), 7.35 (2H, d, ^3J = 16.0 Hz, H^7 or H^8). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{43}H_{31}N_3$: 591.70 $[M+2H]^+$, found: 591.35. Elemental analysis: calculated: %C 87.58, %H 5.30, %N 7.13; found: %C 87.55, %H 5.25, %N 7.19.



3N,P'SpPy. The synthesis was carried out according to **2,3'-SpPy** with chalcone **3N**,**P'-ch** (150 mg, 0.450 mmol), **SpPy-salt** (130 mg, 0.227 mmol), NH_4OAc (1.13 g, 14.7 mmol) and MeOH (20 mL).Yield: 1.95 % (3.50 mg, 0.0044 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.85 (2H, d, ^4J = 2.0 Hz, H$^{3'}$), 8.48 (2H, d, ^3J = 9.5 Hz, H^3 and H^5), 8.32 (2H, d, ^3J = 8.0 Hz, H$^{4'''}$ or H$^{6'''}$), 8.27 (2H, d, ^3J = 8.0 Hz, H$^{4'''}$ or H$^{6'''}$), 8.23-8.19 (6H, m, H$^{4'}$, H$^{6'''}$ and H^{Pyren}), 8.15-8.11 (4H, m, H^{Pyren}), 8.09-8.05 (7H, m, H^4 and H^{Pyren}), 7.70 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{5'''}$), 6.78 (2H, dd, ^3J = 5.0 Hz, ^3J = 8.0 Hz, H$^{6''}$), 6.36 (2H, dd, ^3J = 7.0 Hz, ^3J = 10.5 Hz, H$^{4''}$ or H$^{5''}$), 5.52 (2H, dd, ^3J = 7.0 Hz, ^3J = 10.5 Hz, H$^{4''}$ or H$^{5''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{57}H_{33}N_5$: 788.83 $[M+H]^+$, found: 788.84. Not enough material for an elemental analysis.

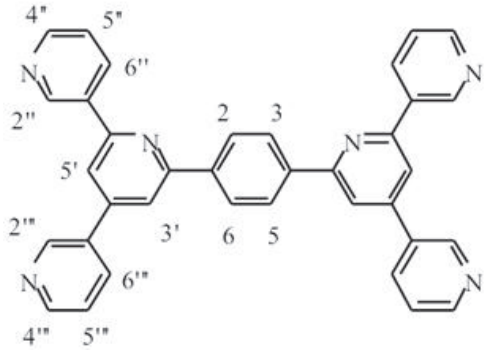


2,Ph'-Ph-bar-bell-compound. 2-Pyridylchalcone **2N**,**Ph'-ch** (382 mg, 1.83 mmol), NH_4OAc (3.20 g, 41.5 mmol), and phenyl bispyridinium iodine salt (**Ph-BBC-salt**) (491 mg, 0.858 mmol) were suspended in MeOH (15.0 mL) and refluxed for 24 h. A beige solid was filtered and washed with MeOH (20 mL). A yellow-greenish solid was recrystallized from MeOH (30 mL). Yield: 54.3% (251 mg, 0.465 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 8.79 (2H, m, ^4J = 1.5 Hz, ^4J = 2.0 Hz, ^3J = 4.5 Hz, H$^{6''}$), 8.76 (2H, d, ^3J = 8.0 Hz, H$^{3'''}$), 8.75 (2H, d, ^4J = 1.5 Hz, H$^{5'}$), 8.44 (4H, s, H^2, H^3, H^5 and H^6), 8.12 (2H, d, ^4J = 1.5 Hz, H$^{3'}$), 7.95-7.89 (6H, m, H$^{5''}$ and H^{Phenyl}), 7.61-7.58 (4H, m,H^{Phenyl}), 7.54 (2H, tt, ^4J = 1.5 Hz, ^3J = 7.5 Hz, H^{Phenyl}), 7.39 (2H, ddd, ^4J = 1.0 Hz, ^3J = 4.5 Hz, ^3J = 7.5 Hz, H$^{4''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): δ = 156.7, 156.6, 156.4, 150.6, 149.5, 140.2, 138.9, 137.3, 129.5, 129.4, 127.8, 127.6, 124.3, 121.8, 118.8, 118.2. MALDI-TOF: calculated *m/z* for $C_{38}H_{26}N_4$: 539.62 $[M+H]^+$, found: 539.83. Elemental analysis: calculated: %C 84.73, %H 4.87, %N 10.40; found: %C 84.80, %H 4.91, %N 10.54.

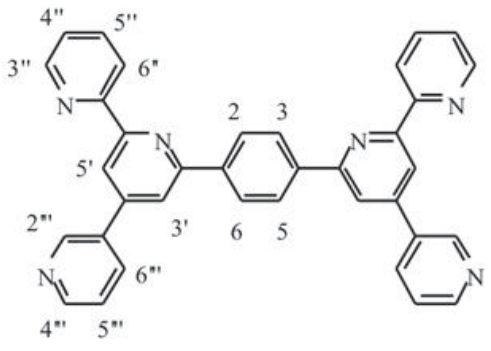


Ph,3'-Ph-bar-bell-compound. 3'-Pyridylchalcone (**Ph,3N'-ch**) (200 mg, 0.956 mmol) NH_4OAc (1.70 g, 22.1 mmol) and **Ph-**

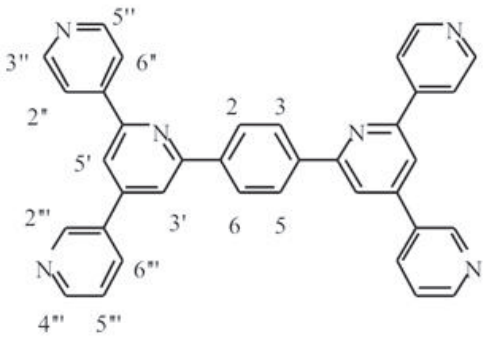
BBC-salt (300 mg, 0.524 mmol) were suspended in MeOH (9 mL) and refluxed for 24 h. A solid was filtered, washed with MeOH and dried under vacuum. Yield: 74.4% (210 mg, 0.389 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.03 (2H, d, ^4J = 2.0 Hz, H$^{2'''}$), 8.75 (2H, dd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, H$^{4'''}$), 8.42 (4H, s, H^2, H^3, H^5 and H^6), 8.27 (4H, d, ^3J = 7.0 Hz, H$^{2''}$ and H$^{6''}$), 8.11 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{6'''}$), 7.99 (2H, s, H^3 or H$^{5'}$), 7.93 (2H, s, H^3 or H$^{5'}$), 7.59 (4H, t, ^3J = 7.0 Hz, H$^{3''}$ and H$^{5''}$), 7.54-7.52 (2H, m, H$^{4''}$ and H$^{5'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d$_2$): δ = 158.0, 157.3, 150.4, 148.4, 147.4, 140.1, 139.3, 135.0, 134.8, 129.8, 129.2, 127.8, 127.5, 124.3, 120.6, 117.5, 117.3, 99.8. MALDI-TOF: calculated *m/z* for $C_{38}H_{26}N_4$: 540.63 $[M+2H]^+$, found: 540.80. Elemental analysis: calculated: %C 84.73, %H 4.87, %N 10.40; found: %C 84.84, %H 4.92, %N 10.58.



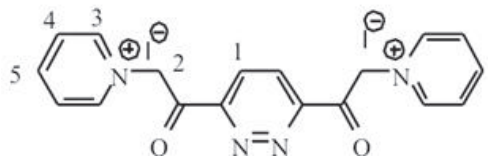
3,3'-Ph-bar-bell-compound. The synthesis was carried out according to Ph,3'-Ph-bar-bell-compound (**Ph,3N'-Ph-BBC**) with 3,3'-dipyridylchalcone (**3,3'-ch**) (190 mg, 0.904 mmol), NH_4OAc (2.10 g, 27.2 mmol) and **Ph-BBC-salt** (242 mg, 0.423 mmol). Yield: 17.7% (40.5 mg, 0.0749 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.48 (2H, d, ^4J = 1.5 Hz, H$^{2''}$), 9.08 (2H, d, ^4J = 2.0 Hz, H^2), 8.80 (2H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{4''}$ or H$^{6''}$), 8.76 (2H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, H$^{4''}$ or H$^{6''}$), 8.57 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{4'''}$), 8.43 (4H, s, H^2, H^3, H^5 and H^6), 8.10 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{6'''}$), 8.06 (2H, d, ^4J = 1.0 Hz, H$^{3'}$ or H$^{5'}$), 7.96 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 7.54-7.50 (4H, m, H$^{5''}$ and H$^{5'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{36}H_{24}N_6$: 540.59 $[M+H]^+$, found: 540.86. Elemental analysis: calculated: %C 79.98, %H 4.47, %N 15.55; found: %C 80.09, %H 4.36, %N 15.81.



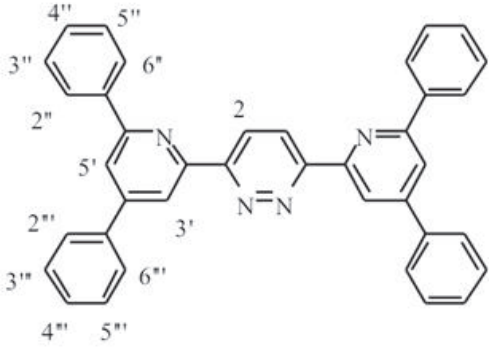
2,3'-Ph-bar-bell-compound. The synthesis was carried out according to **Ph,3N'-Ph-BBC** with 2,3'-dipyridylchalcone (**2,3'-ch**) (200 mg, 0.951 mmol), **Ph-BBC-salt** (270 mg, 0.472 mmol) and NH_4OAc (1.70 g, 22.1 mmol). Yield: 35.2% (90.0 mg, 0.166 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.14 (2H, d, ^4J = 2.0 Hz, H$^{5'}$), 8.81-8.75 (8H, m, H$^{3''}$, H$^{6''}$, H$^{2'''}$ and H$^{4'''}$), 8.45 (4H, s, H^2, H^3, H^5 and H^6), 8.18 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{6'''}$), 8.10 (2H, d, ^4J = 2.0 Hz, H$^{3'}$), 7.95 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, H$^{5''}$), 7.52 (2H, dd, ^3J = 4.5 Hz, ^3J = 8.0 Hz, H$^{5'''}$), 7.42 (2H, ddd, ^4J = 1.0 Hz, ^3J = 4.5 Hz, ^3J = 8.0 Hz, H$^{4''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{36}H_{24}N_6$: 541.59 $[M+H]^+$, found: 541.94. Elemental analysis: calculated: %C 79.98, %H 4.47, %N 15.55; found: %C 80.14, %H 4.38, %N 15.57.



4,3'-Ph-bar-bell-compound. The synthesis was carried out according to **Ph,3N'-Ph-BBC** with 4,3'-dipyridylchalcone (**4,3'-ch**) (200 mg, 0.951 mmol), **Ph-BBC-salt** (270 mg, 0.472 mmol) and NH_4OAc (1.70 g, 22.1 mmol). Yield: 78.7% (201 mg, 0.371 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.09 (2H, dd, ^4J = 1.0 Hz, ^4J = 2.0 Hz, H$^{2'''}$), 8.85 (4H, dd, ^4J = 2.0 Hz, ^3J = 5.0 Hz, H$^{3''}$ and H$^{5''}$), 8.81 (2H, dd, ^4J = 2.0 Hz, ^3J = 5.0 Hz, H$^{4'''}$), 8.45 (4H, s, H^2, H^3, H^5 and H^6), 8.17 (4H, dd, ^4J = 2.0 Hz, ^3J = 5.0 Hz, H$^{2''}$ and H$^{6''}$), 8.12-8.09 (2H, m, H$^{6'''}$), 8.10 (2H, d, ^4J = 2.0 Hz, H$^{3'}$ or H$^{5'}$), 8.01 (2H, d, ^4J = 1.5 Hz, H$^{3'}$ or H$^{5'}$), 7.54 (2H, ddd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, ^3J = 8.0 Hz, H$^{5'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{36}H_{24}N_6$: 542.60 $[M+H]^+$, found: 542.63. Elemental analysis: calculated: %C 79.98, %H 4.47, %N 15.55; found: %C 80.08, %H 4.37, %N 15.69.

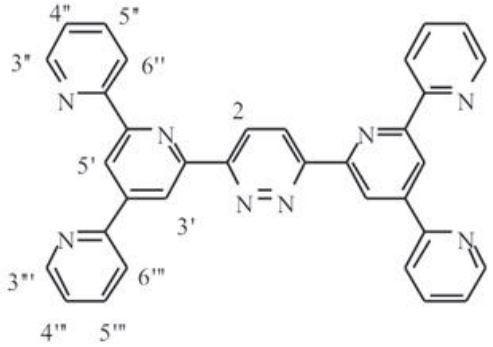


Pyridazine bispyridinium iodine salt. 3,6-Diacetylpyridazine (0.35 g, 2.1 mmol) and iodine (1.2 g, 4.7 mmol) were refluxed in dry pyridine (10 mL) for 4 h. After stirring another 20 h at r.t. a black solid was filtered and washed with MeOH (30 mL), till the washing liquid was colorless. The solid was dried under vacuum. Yield: 34% (0.41 g, 0.71 mmol). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.09-9.07 (4H, m, H^3), 8.80-8.75 (4H, m, H^4), 8.52 (2H, s, H^1), 8.18-8.12 (2H, m, H^5), 6.73 (4H, s, H^2). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. Elemental analysis for $C_{18}H_{16}I_2N_4O_2$: calculated: %C 37.65, %H 2.81, %N 9.76; found: %C 38.02, %H 3.01, %N 9.95.

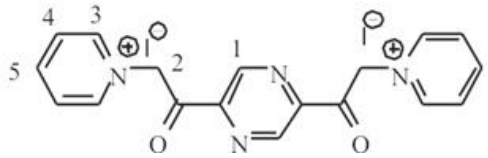


Ph,Ph'-Pyridazine-bar-bell-compound. Chalcone **ch** (72.5 mg, 0.350 mmol), pyridazine bispyridinium iodine salt (**Pyz-BBC-salt**) (100 mg, 0.174 mmol) and NH_4OAc (405 mg, 5.25 mmol) were refluxed in MeOH (8 mL) for 24 h. A solid was filtrated, washed with MeOH and dried under vacuum. Yield: 19.7 % (18.5 mg, 0.0343 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.06 (2H, d, ^4J = 2.0 Hz, H$^{3'}$), 9.00 (2H, s, H^2), 8.31-8.28 (4H, m, H$^{2''}$ and H$^{6''}$), 8.15 (2H, ^4J = 2.0 Hz, H$^{5'}$), 7.95-7.92 (4H, m, H^{Phenyl}), 7.64-7.59 (8H, m, H^{Phenyl}), 7.57-7.54 (4H, m, H^{Phenyl}). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{38}H_{26}N_4$:

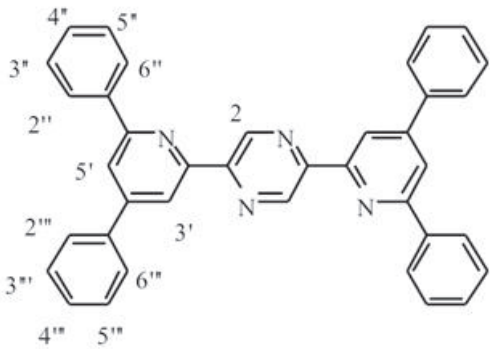
539.62 $[M+H]^+$, found: 539.70. Elemental analysis: calculated: %C 84.73, %H 4.87, %N 10.40; found: %C 84.50, %H 4.86, %N 10.62.



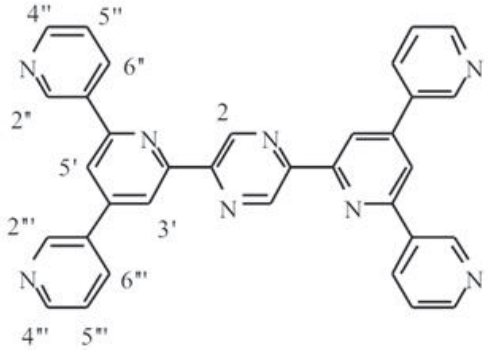
2,2'-Pyridazine-bar-bell-compound. 2,2'-Dipyridylchalcone (**2**,**2'-ch**) (0.15 g, 0.71 mmol), **Pyz-BBC-salt** (0.20 g, 0.34 mmol) and NH_4OAc (1.4 g, 18 mmol) were refluxed in MeOH (8.0 mL) for 3 d. A solid was filtrated, washed with MeOH and dried under vacuum for 6 h at 180 °C. Yield: 27% (51 mg, 0.092 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.03 (2H, d, ^4J = 1.5 Hz, $H^{3'}$ or $H^{5'}$), 8.89-8.87 (2H, m, $H^{3''}$, $H^{6''}$ or $H^{3'''}$), 8.82-8.80 (2H, m, $H^{3''}$, $H^{6''}$ or $H^{3'''}$), 8.79-8.76 (2H, m, $H^{3''}$, $H^{6''}$ or $H^{3'''}$), 8.61-8.60 (2H, d, ^4J = 1.5 Hz, $H^{3'}$ or $H^{5'}$), 8.49 (2H, s, H^2), 8.09-8.08 (2H, m, $H^{6'''}$), 7.94 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, $H^{5''}$ or $H^{5'''}$), 7.92 (2H, dt, ^4J = 2.0 Hz, ^3J = 8.0 Hz, $H^{5''}$ or $H^{5'''}$), 7.43 (2H, ddd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, ^3J = 8.0 Hz, $H^{4''}$ or $H^{4'''}$), 7.41 (2H, ddd, ^4J = 1.0 Hz, ^3J = 5.0 Hz, ^3J = 8.0 Hz, $H^{4''}$ or $H^{4'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{34}H_{22}N_8$: 543.57 $[M+H]^+$, found: 543.49. Elemental analysis: calculated: %C 75.26, %H 4.09, %N 20.65; found: %C 75.09, %H 4.17, %N 20.73.



*Pyrazine bispyridinium iodine salt***.** 1,4-Diacetylpyrazine (330 mg, 2.01 mmol) and iodine (1.02 g, 4.02 mmol) were suspended in dry pyridine (5.2 mL) and refluxed for 3 h in an Ar-atmosphere. After stirring 20 h at r.t. a solid was filtrated, washed with EtOH (30 mL) and air-dried for 1 h to yield a golden brown product. Yield: 91.8% (1.06 g, 1.85 mmol). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.49 (2H, s, H^1), 9.03 (4H, m, H^3), 8.78 (2H, m, H^5), 8.33 (4H, m, H^4), 6.54 (4H, s, H^2). ^{13}C NMR (400 MHz, DMSO-d_6): δ = 190.2, 147.8, 146.6, 146.2, 142.2, 127.7, 66.4. MS (CI): calculated *m/z* for $C_{18}H_{16}I_2N_4O_2$: 165.15 $[M-2C_6H_5N-2I+H]^+$, found: 164.87. Elemental analysis: calculated for $C_{18}H_{16}I_2N_4O_2$: %C 37.65, %H 2.81, %N 9.76; found: %C 37.91, %H 2.99, %N 9.90.



Ph,Ph'-Pyrazine-bar-bell-compound. Chalcone **ch** (221 mg, 1.07 mmol), NH_4OAc (1.92 g, 24.9 mmol) and pyrazine bispyridinium iodine salt (**Pdz-BBC-salt**) (300 mg, 0.523 mmol) were suspended in MeOH (8.5 mL) and reflluxed for 20 h. A dark solid precipitated, was centrifuged and dried under vacuum. Yield: 3.0% (8.5 mg, 0.015 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 10.00 (2H, s, H^2), 8.74 (2H, d, ^4J = 1.0 Hz, $H^{3'}$), 8.31 (4H, d, ^3J = 7.5 Hz, $H^{2''}$ and $H^{6''}$), 8.10 (2H, d, ^4J = 1.5 Hz, $H^{5'}$), 7.89 (4H, d, ^3J = 7.0 Hz, H^{Phenyl}), 7.62-7.53 (12H, m, H^{Phenyl}). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): δ = 157.7, 155.0, 151.1, 150.8, 142.6, 139.4, 138.7, 129.5, 129.4, 129.3, 129.0, 127.45, 127.39, 119.0, 118.4. MALDI-TOF: calculated *m/z* for $C_{39}H_{25}N_9$: 539.62 $[M+H]^+$, found: 539.82. Not enough material for an elemental analysis.



3,3'-Pyrazine-bar-bell-compound. 3,3'-Dipyridylchalcone (**3**,**3'-ch**) (225 mg, 1.07 mmol), NH_4OAc (1.92 g, 24.9 mmol), and **Pdz-BBC-salt** (300 mg, 0.523 mmol) were suspended in MeOH (8.5 mL) and refluxed for 20 h. A dark solid precipitated, was centrifuged and dried under vacuum. Yield: 6.41% (18.2 mg, 0.0335 mmol). ^{1}H NMR (500 MHz, 100 °C, TCE-d_2): δ = 9.98 (2H, s, H^2), 9.49 (2H, d, ^4J = 2.0 Hz, $H^{3'}$, $H^{2''}$ or $H^{2'''}$), 9.13 (2H, d, ^4J = 2.0 Hz, $H^{3'}$, $H^{2''}$ or $H^{2'''}$), 8.81 (2H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, $H^{4''}$ or $H^{4'''}$), 8.80 (2H, d, ^4J = 2.0 Hz, $H^{3'}$, $H^{2''}$ or $H^{2'''}$), 8.79 (2H, dd, ^4J = 1.5 Hz, ^3J = 4.5 Hz, $H^{4''}$ or $H^{4'''}$), 8.58 (2H, dt, ^3J = 8.0 Hz, ^4J = 2.0 Hz, $H^{6''}$), 8.17 (2H, dt, ^3J = 8.0 Hz, ^4J = 2.0 Hz, $H^{6'''}$), 8.09 (2H, d, ^4J = 2.0 Hz, $H^{5'}$), 7.55-7.52 (4H, m, $H^{5''}$ and $H^{5'''}$). ^{13}C NMR (500 MHz, 100 °C, TCE-d_2): Solubility too low. MALDI-TOF: calculated *m/z* for $C_{34}H_{22}N_8$: 543.57 $[M+H]^+$, found: 543.76. Elemental analysis: calculated: %C 75.26, %H 4.09, %N 20.65; found: %C 74.81, %H 4.22, %N 20.51.

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