Supporting information for article

Donor (HO-) and Acceptor (Nitro-) Substituted BODIPY for the Bathochromic Solvent Turn-on Fluorescence Dye

Robertson Akrofi,[a] Suci Meng,[a,b] Xinyi Dong,[a] Qiuyun Chen,[a@1] Laihai Huang,[a] Yuanyuan Fang,[a] Lingling Qu,[a] and Xu Liang[a@2]

[a]*School of the Environment and Safety Engineering, School of Chemistry and Chemical Engineering, Jiangsu University, 212013 Zhenjiang, P. R. China*

[b]*Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, 210093 Nanjing, P. R. China*

[@1]*Corresponding author E-mail: chenqy@ujs.edu.cn*

[@2]*Corresponding author E-mail: Liangxu@ujs.edu.cn*

Experimental Section

Chemicals and Instrumentation

2,4-Dimethylpyrrole (98 %), 4-nitrobenzaldehyde (9 8%), *N*-iodosuccinimide (NIS, 98 %), 5-(4-formylphenyl)boronic acid (98 %), sodium borohydride (98 %), boron trifluoride etherate (98 %, $BF_3.OEt_2$, 46.5 %), $Pd(PPh_3)_4$, K_2CO_3, were purchased from Energy Chemical Reagent Co. Ltd. 4-Hydroxymethylphenylboronic acid, 5,5-difluoro-2-iodo-1,3,7,9-tetramethyl-10-(4-nitrophenyl)-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (NO_2-BDPY-I), 5,5-difluoro-2-iodo-1,3,7,9-tetramethyl-10-(4-nitrophenyl)-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2] diazaborinine (A), (4-(5,5-difluoro-1,3,7,9-tetramethyl-10-(4-nitrophenyl)-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2] diazaborinin-2-yl)phenyl)methanol were synthesized according to literature procedures.[13] FT-IR characterizations were performed using a Nicolet Nexus 470 FT-IR spectrophotometer in the wavenumber range of 400-4000 cm^{-1}. The electronic absorption spectrum was recorded using a UV-2450 UV-Vis spectrophotometer at room temperature. Fluorescence measurements were performed on a fluorescence spectrofluorometer Model CARY Eclipse (VARIAN, USA), a 1.0 cm quartz cell (slit width = 2.5 nm) was used to detect the λ = 520-650 nm, which excited at λ = 500 nm. The Instantaneous attenuation between λ = 570-580 nm could be explained the limited life-time of light source. The electrospray mass spectra (ES-MS) were determined on a Finnigan LCQ mass spectrograph. The ^{1}HNMR (400 MHz) data were recorded on a Bruker AVANCE II 400 MHz spectrometer using $CDCl_3$ as solvent. The chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. TEM was performed at room temperature on a JEOLJEM-200CX transmission electron microscope using an accelerating voltage of 200 kV.

Fluorescence Titration

BDPPhOH solution (10 μM) in DCM was diluted with the different solvents to measure the emission change at 550 nm. The quantum yield of both the samples relative to Rhodamine B (Qr) was calculated according to equation 1.

$$Q_s = Q_r \left(\frac{A_r}{A_S}\right)\left(\frac{E_S}{E_r}\right)\left(\frac{n_S}{n_r}\right)^2 \quad \text{---------- (1)}$$

In the above equation, 'Ar' and 'As' represent the sample and the standard. Q_r, Q_s, E_s and E_r n_s and n_r, respectively, represent the fluorescence quantum yield, the molar absorption coefficient at steady state and the refractive index of the solvents optically matched solutions were used (the solutions of the sample and the standard should give same absorbance at the excitation wavelength).

NMR Spectra

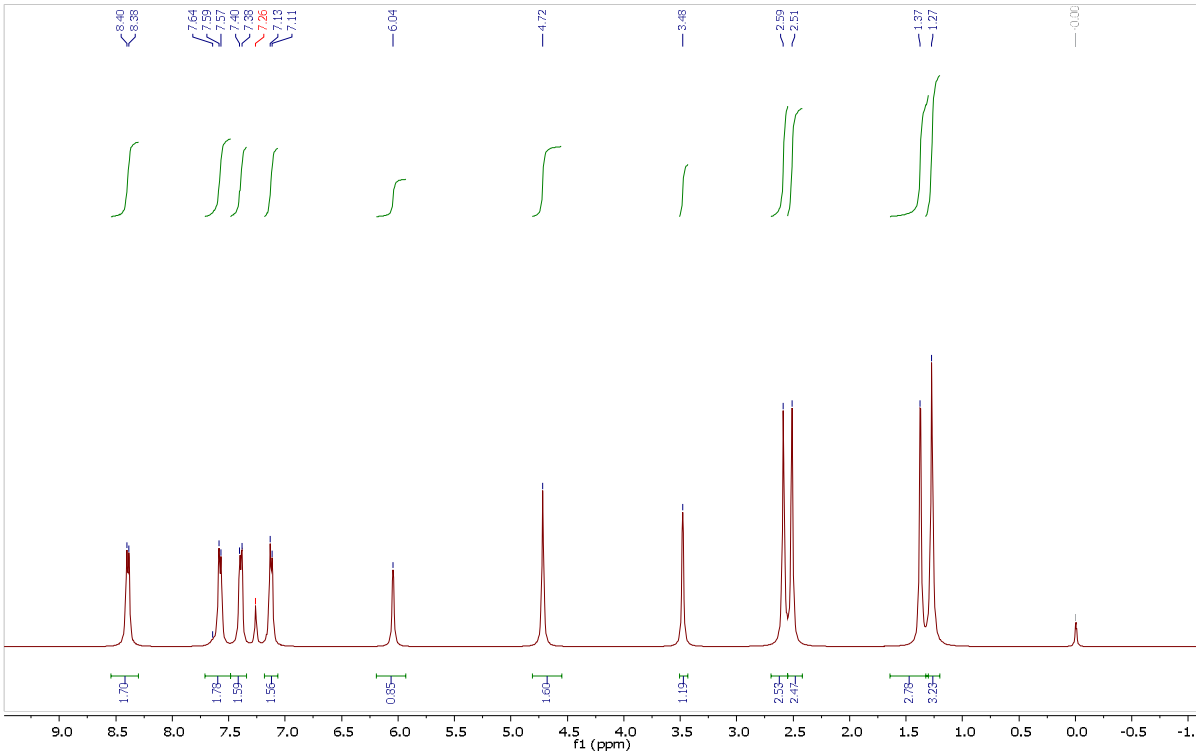


Figure S1. The ^{1}HNMR spectrum of **BDPPhOH** in chloroform ($CDCl_3$).

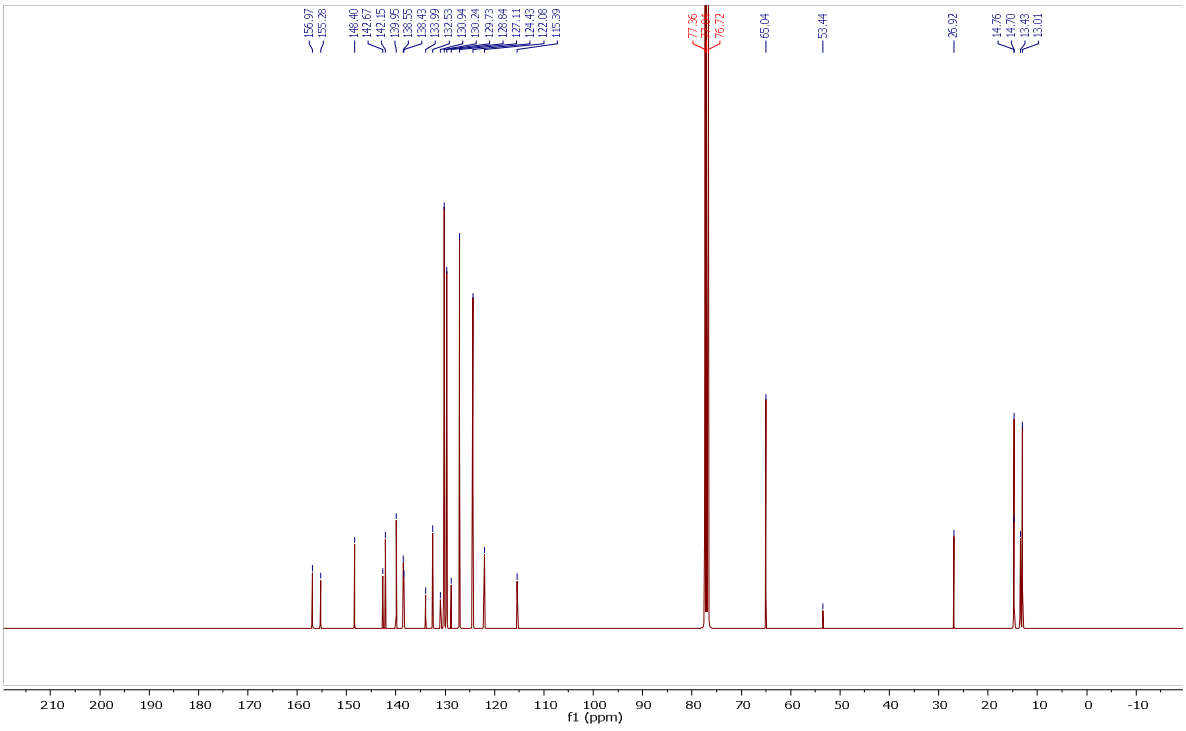


Figure S2. The ^{13}CNMR spectrum of compound **BDPPhOH** in chloroform ($CDCl_3$).

ESI-mass Spectra

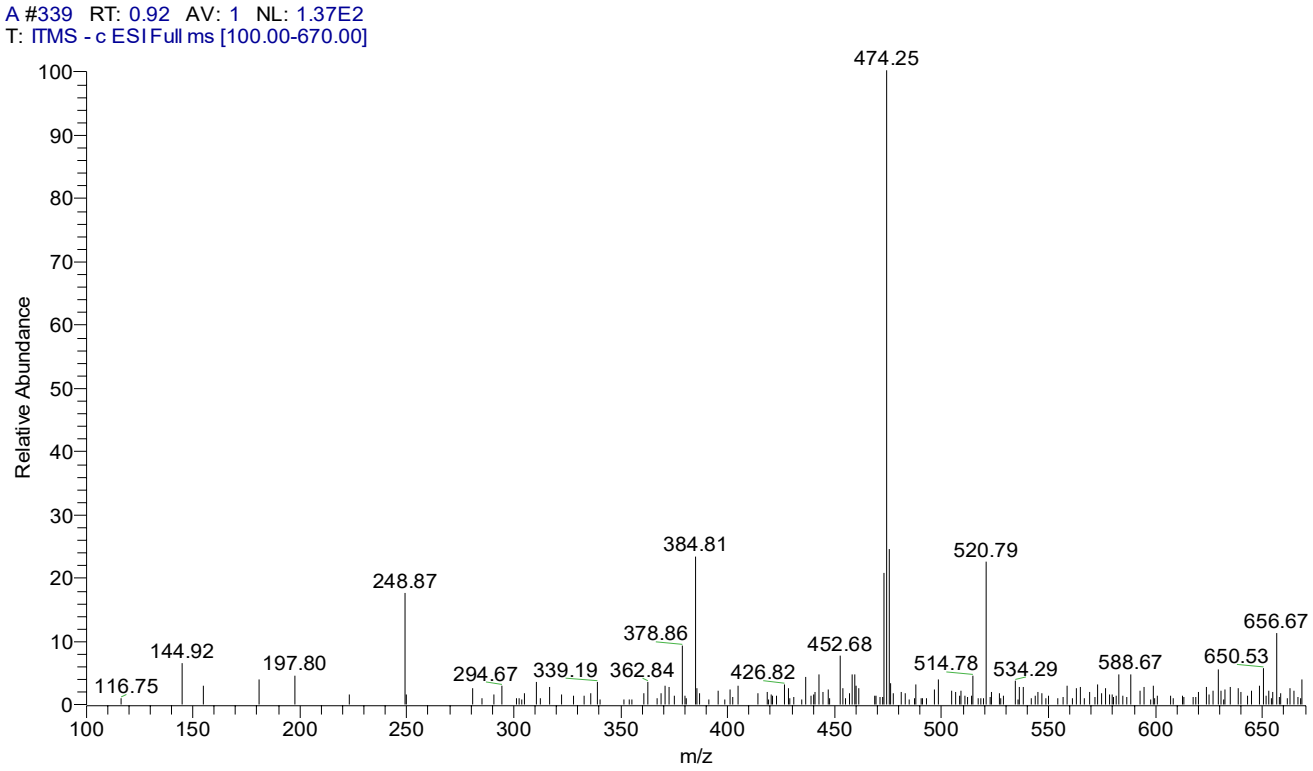


Figure S3. The ESI-MS of **BDPPhOH** in CH_3CN. [M-H] *m/z*= 474.25 in the ESI-Negative mode.

TD-DFT Calculations

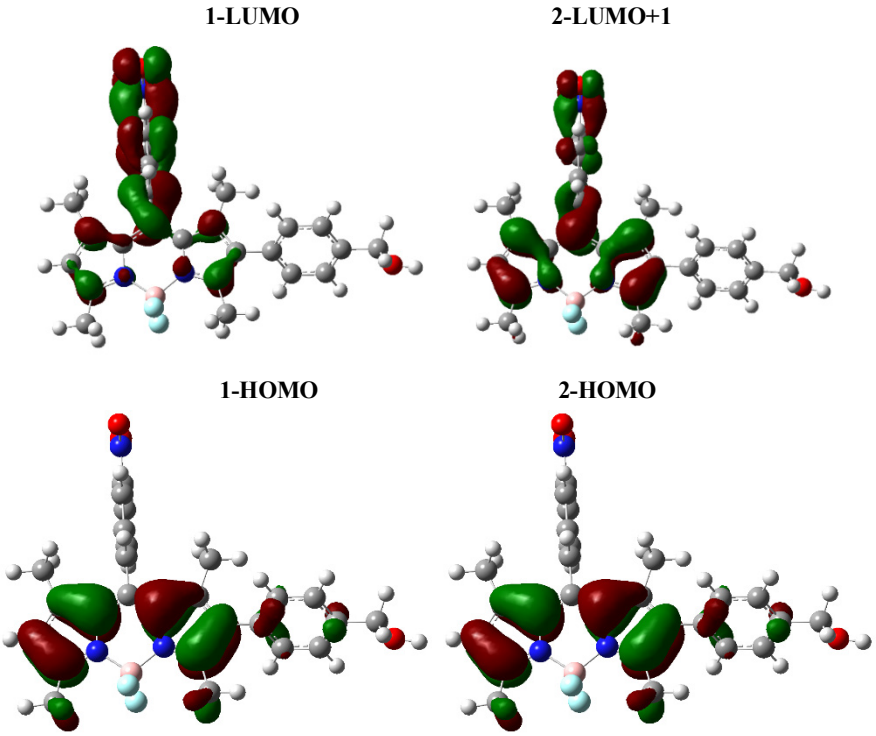


Figure S4. HOMO and LUMO of monomeric **BDPPhOH** compound *via* intermolecular H-bonding in DFT calculation. The molecular orbitals are obtained through DFT calculations at the B3LYP/6-31G** level.

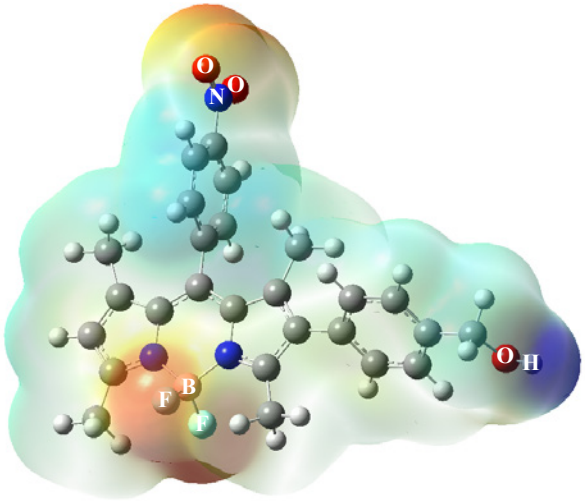


Figure S5. Plot of electrostatic potential of **BDPPhOH** through B3LYP/6-31G** calculation. The red parts indicate the electronegativity and the blue parts indicate the electropositivity.

Electrochemistry

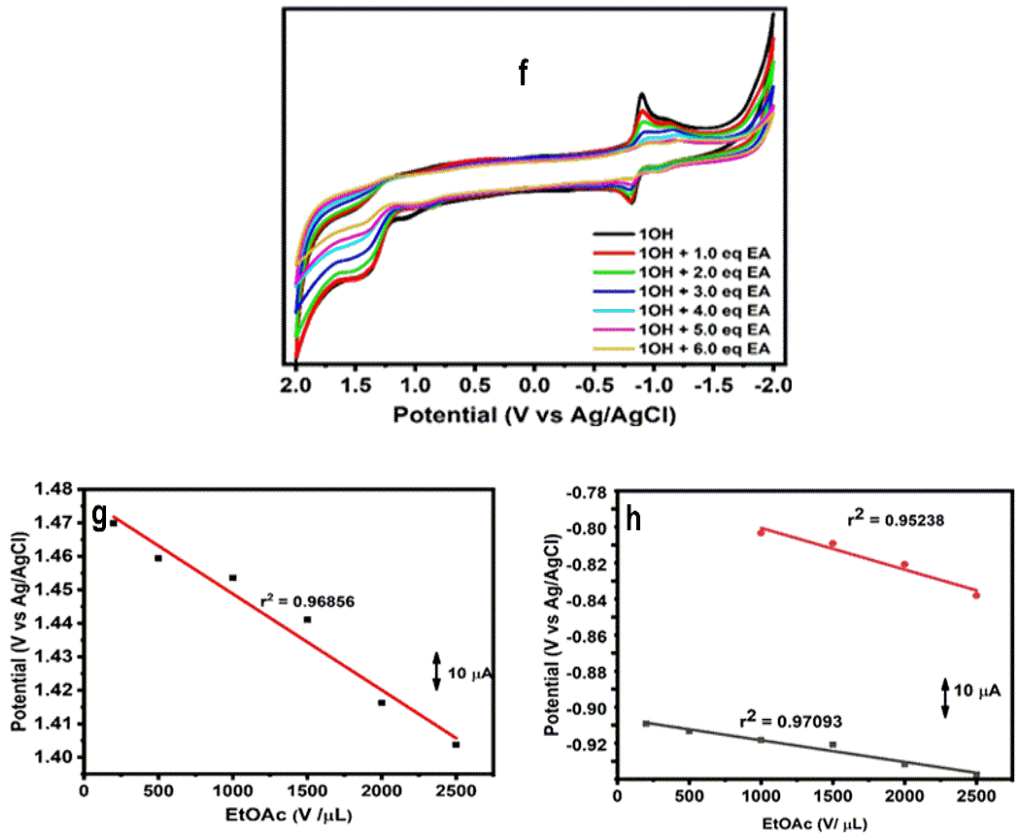


Figure S6. (ii): f)Time independent electrochemical changes of cv as equivalent EA is added to **BDPPhOH** ($2.0 \cdot 10^{-5}$ M) (from 1 to 7 equivs, v/v). Plots of g) anodic and h) cathodic currents showing linear relationship of changes in **BDPPhOH** (DCM) and EA (µL) for both Conditions: 50 mV s^{-1} scan rate (in exceptions of d, e and f), at 25 ^{0}C, solvent: CH_2Cl_2 in 0.1M TBAP.

Mechanism

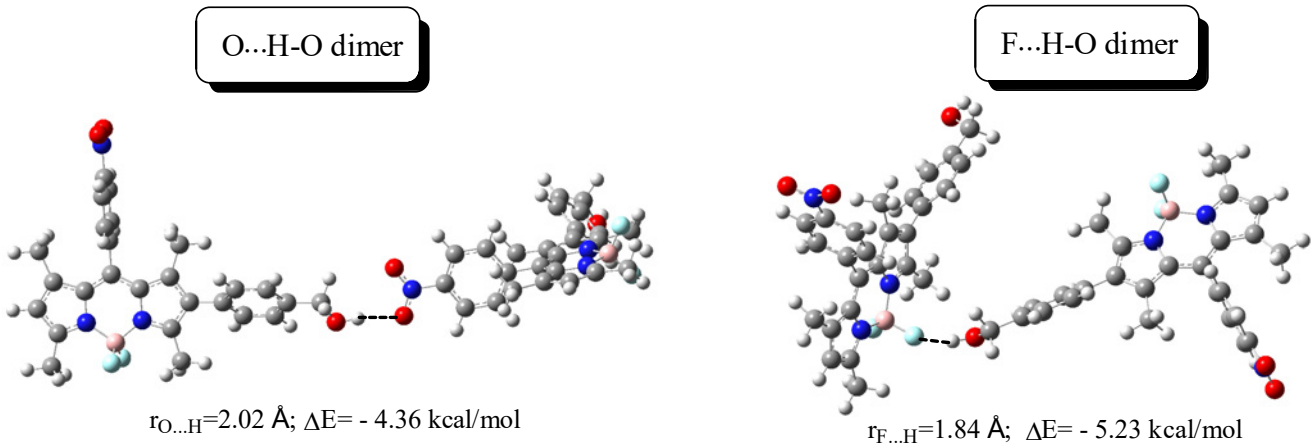
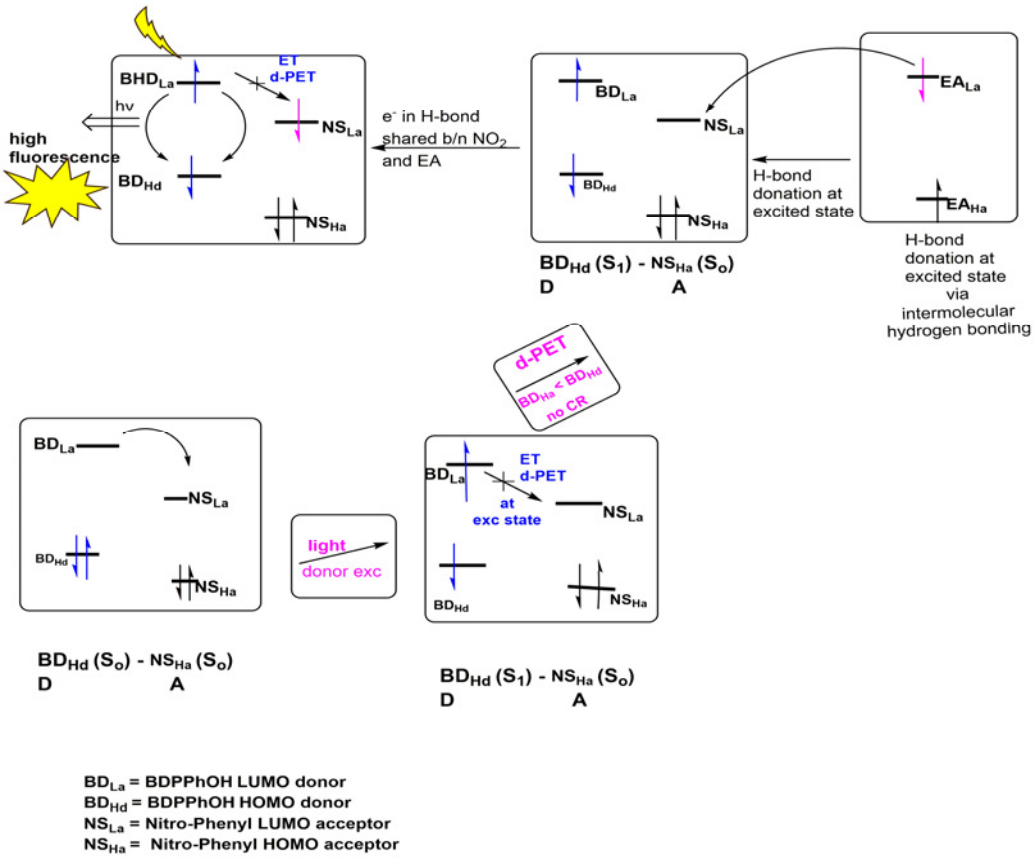


Figure S7. The optimized hydrogen-bonded O…H-O and F…H-O dimers as well as their intermolecular interactions at the B3LYP/6-31G** level.



Scheme S1. BDPPhOH at molecular orbital level d-PET process blocking mechanism for the donor and acceptor; H-EA bond donor through bonding turns-ON fluorescence.

Table S1. The wavelengths, oscillator strengths (f), and the main transitions of **BDPPhOH** monomer, O…H-O dimmer, and F…H-O dimer through TD-DFT calculations at the B3LYP/6-31G** level.

	Longest absorption peak			Strongest absorption peak		
	Wavelengh	f	main transition	wavelength	f	main transition
monomer	524 nm	0.006	HOMO→LUMO	443 nm	0.424	HOMO→LUMO+1
O…H-O dimer	636 nm	0.002	HOMO-1→LUMO	540 nm	0.006	HOMO→LUMO+2
F…H-O dimer	528 nm	0.008	HOMO→LUMO+2	451 nm	0.564	HOMO→LUMO+3

Table S2. The frontier molecular orbital energies of **BDPPhOH** monomer and the F…H-O and O…HO dimers.

	monomer	F…H-O dimer	O…HO dimer
LUMO	-0.09942	-0.10493	-0.11980
HOMO	-0.20267	-0.20115	-0.19712
HOMO-LUMO	0.10325	0.09622	0.07732