

Supporting Information for

Turn-on fluorescence sensing of vapor phase electron donating amines via tetraphenylporphyrin or metallophenylporphrin doped polyfluorene

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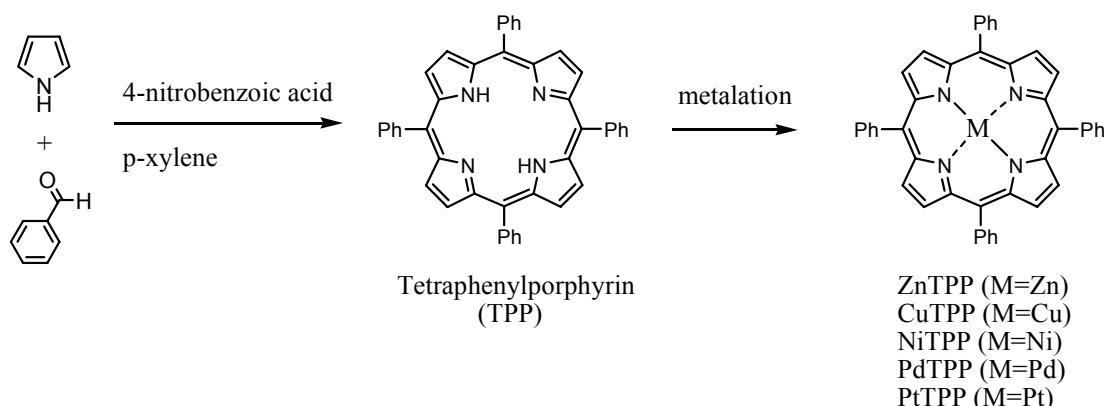
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General Methods and Instrumentation: The ¹H NMR spectra were obtained from a Bruker DRX500 instrument, and tetramethylsilane (TMS) was used as an internal standard. Mass spectra were recorded on a BIFLEX III MALDI-TOF (Bruker Daltonics Inc.) mass spectrometer. UV-vis absorption and fluorescence spectra were performed on a Jasco V-670 spectrophotometer and a Jasco FP 6500 spectrometer, respectively. Pristine PFO film, TPP and MTPP quenched PFO films on (10×20 mm) quartz plates were spin-casted using 2000 rpm from their toluene solutions (PFO, 3.8×10^{-3} M; TPP or MTPP, 4.8×10^{-5} M), and placed under vacuum overnight before use. Cyclic voltammetry experiments were performed with a CH Instruments electrochemical analyzer. The electrochemical behavior of TPP, MTPP and PFO was investigated by cyclic voltammetry (CV) with a standard three electrodes (a glassy carbon working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode) electrochemical cell in 0.1 M tetra-n-butylammonium

hexafluorophosphate (Bu_4NPF_6) in acetonitrile solution under nitrogen with a scanning rate of 100 mV/s at room temperature. The fluorescence response of TPP and MTPP quenched PFO films to the vapors of various analytes was progressed by inserting the films into sealed vials (6.75 ml) at room temperature containing cotton and analytes, which prevents direct film analyte contact and help to maintain a constant vapor pressure. The fluorescence time-course responses were recorded immediately after exposing the films to analytes by front-face (30°) detection.

Materials: Polydioctylfluorene (PFO) was purchased from Synwit Technology Co., Ltd, $M_h=33000$, $M_w=92000$ by GPC. Methamphetamine (MAPA) was obtained from Institution of Forensic Science, The Criminal Department of Shanghai Public Security Bureau. All solvents and reagents were obtained from commercial sources and used as received. Tetraphenylporphyrin (TPP) and MetalloTetraphenylporphyrins (MTPP, M = Zn, Cu, Ni, Pd, Pt) were synthesized according to literature procedures.



Synthesis

TPP and MTPP were synthesized according to the literature.

Tetraphenylporphyrin (TPP).^[1] To a refluxing mixture of benzaldehyde (8.37 g, 79.0 mmol) and 4-nitrobenzoic acid (3.7 g) in p-xylene (180 ml) 5.4 ml pyrrole (5.29 g, 79.0 mmol) was added. The resulting mixture was refluxed for about 3h, and then the solvent was removed by distillation at 160 °C, the residue was purified by column chromatography on neutral Al₂O₃ using CH₂Cl₂ as eluent. The crude product was recrystallized in CH₂Cl₂/MeOH to get purple crystal (4 g, yield 33%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.85 (s, 8H), 8.21 (d, 8H, *J*=6.5Hz), 7.72 (m, 12H), -2.77 (br, 2H). MALDI-TOF MS: m/z 615.5.

Metalation of TPP ^[2]

ZnTPP. A saturated solution of Zn(OAc)₂ (0.12 g, 0.655 mmol) in MeOH was added to a solution of TPP (0.3 g, 0.488 mmol) in CHCl₃ (30ml), and the resulting mixture was stirred for 1h. After the complete metalation was confirmed by TLC, the mixture was poured into 100 ml water and extracted with CHCl₃, the organic layer was washed with water and brine and dried over anhydrous MgSO₄. The solvent was removed and the residue was recrystallized in CH₂Cl₂/MeOH to get purple powder (0.31 g, yield 94%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.95 (s, 8H), 8.21 (d, 8H, *J*=8Hz), 7.73 (m, 12H). MALDI-TOF MS: m/z 676.2.

CuTPP. A saturated solution of Cu(OAc)₂ (0.13 g, 0.714 mmol) in MeOH was added to a solution of TPP (0.3 g, 0.488 mmol) in CHCl₃ (30ml), and the resulting mixture was refluxed for 3 h in the dark. The mixture was poured into 100 ml water and extracted with CHCl₃, the

organic layer was washed with brine and then dried over anhydrous MgSO₄. The solvent was removed and the residue was recrystallized in CH₂Cl₂/MeOH to get purple crystal (0.30 g, yield 91%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.64 (br, 12H), 7.49 (br, 16H). MALDI-TOF MS: m/z 675.2.

NiTPP. A solution of TPP (0.3 g, 0.488 mmol) in toluene was refluxed with Ni(acac)₂ (0.17 g, 0.659 mmol) for 1 day in the dark. After the complete metalation was confirmed by TLC, the mixture was poured into 100 ml water and extracted with CHCl₃, the organic layer was washed with water and brine and dried over anhydrous MgSO₄. The solvent was removed and the residue was recrystallized in CHCl₃/MeOH to get purple crystal (0.29 g, yield 88%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.75 (s, 8H), 8.01 (d, 8H, *J*=6.0Hz), 7.66 (m, 12H). MALDI-TOF MS: m/z 670.2.

PdTPP. A solution of TPP (0.3 g, 0.488 mmol) in 30 ml CHCl₃ was stirred in the presence of Pd(OAc)₂ (0.16 g, 0.714 mmol) powder at 40 °C for 2 days in the dark. After the complete metalation was confirmed by TLC, the mixture was poured into 100 ml water and extracted with CHCl₃, the organic layer was washed with water and brine and dried over anhydrous MgSO₄. The solvent was removed and the residue was recrystallized in CH₂Cl₂/MeOH to get red powder (0.33 g, yield 94%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.81 (s, 8H), 8.16 (d, 8H, *J*=6.5Hz), 7.72 (m, 12H). MALDI-TOF MS: m/z 718.4.

PtTPP. To a refluxing mixture of TPP (0.3 g, 0.488 mmol) in benzonitrile (40 ml) PtCl₂ (0.16 g, 0.601 mmol) was added under Ar atmosphere. The resulting mixture was refluxed for about

6 h, and stopped when the complete metalation was confirmed by TLC. After the removal of benzonitrile, the mixture was washed with 100 ml water and extracted with CHCl_3 , the organic layer was dried over anhydrous MgSO_4 . The solvent was removed and the residue was recrystallized in $\text{CHCl}_3/\text{MeOH}$ to get red powder (0.30 g, yield 76%). ^1H NMR (500 MHz, CDCl_3 , ppm) δ 8.75 (s, 8H), 8.14 (d, 8H, $J=6.0\text{Hz}$), 7.71 (m, 12H). MALDI-TOF MS: m/z 807.4.

Figures and Tables

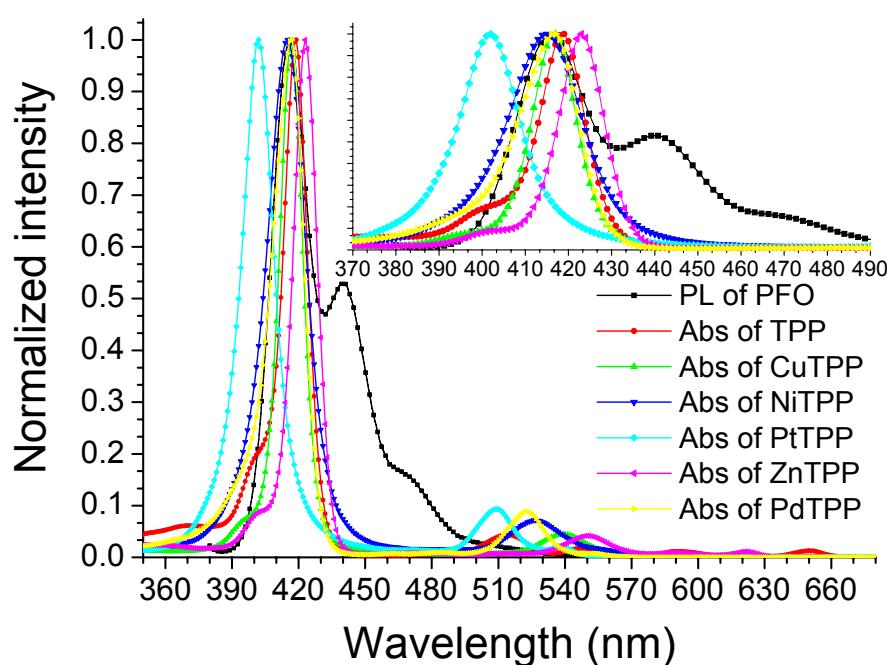


Figure S1. Absorption spectra of TPP or MTPP, and emission spectra of PFO in toluene. (TPP or MTPP, $1.3 \times 10^{-6}\text{M}$; PFO, $3.8 \times 10^{-6}\text{M}$, excitation with 370 nm) The inset is corresponding spectra around maximum peak.

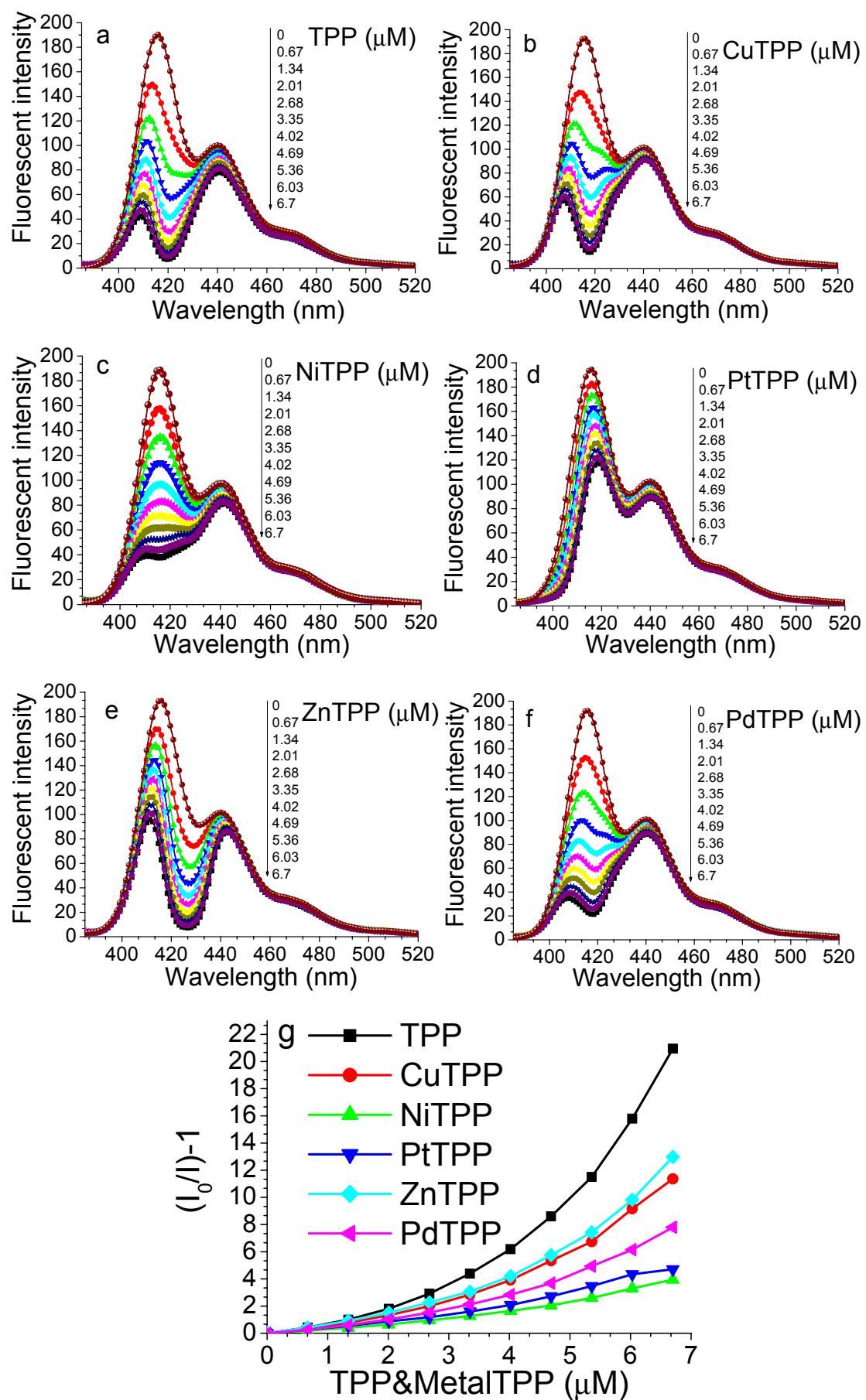


Figure S2. The fluorescence emission spectra of PFO (3.8×10^{-6} M, toluene) with successive addition of TPP (a), CuTPP (b), NiTPP (c), PtTPP(d), ZnTPP (e), PdTPP (f) (0-6.7 μM), the excitation wavelength was at 370 nm. (g) Stern-Volmer plots of PFO for TPP and MTPP in toluene (measured at wavelength of their maximum absorption), Quenching constants (Ksv) of TPP and CuTPP, NiTPP, PtTPP, ZnTPP, PdTPP measured according to the linear part of Stern-Volmer plots were (10^6 M⁻¹): 7.04, 3.44, 1.00, 0.92, 4.14, 2.14, respectively. The concentrations of the PFO were all at 3.8×10^{-6} M, and the excitation wavelength was 370 nm. Quenching constants (Ksv) of TPP and MTPP were determined from the Stern-Volmer equation:^[3]

$$I_0/I = 1 + K_{sv} [Q]$$

Only the emission of PFO at wavelength of Soret absorption peak of TPP or MTPP was significantly quenched (Figure S2) indicating radiative energy transfer that involves the emission of a photo by PFO and subsequent reabsorption by TPP made a main contribution to the apparent quenching. Moreover, Ksv values of TPP, CuTPP, NiTPP and PdTPP with the similar absorption peaks were in consisting with the absorption ability (Table S2) testified this radiative energy transfer quenching mechanism. The upward non-linear curvature of Stern-Volmer plots (Figure S2) suggested nonradiative energy transfer resulting from direct resonance of excited PFO and unexcited TPP or MTPP took place, for there are always TPP (MTPP) molecules within Förster radius distance from one of the PFO molecules when the TPP (MTPP) concentration increased.^[4]

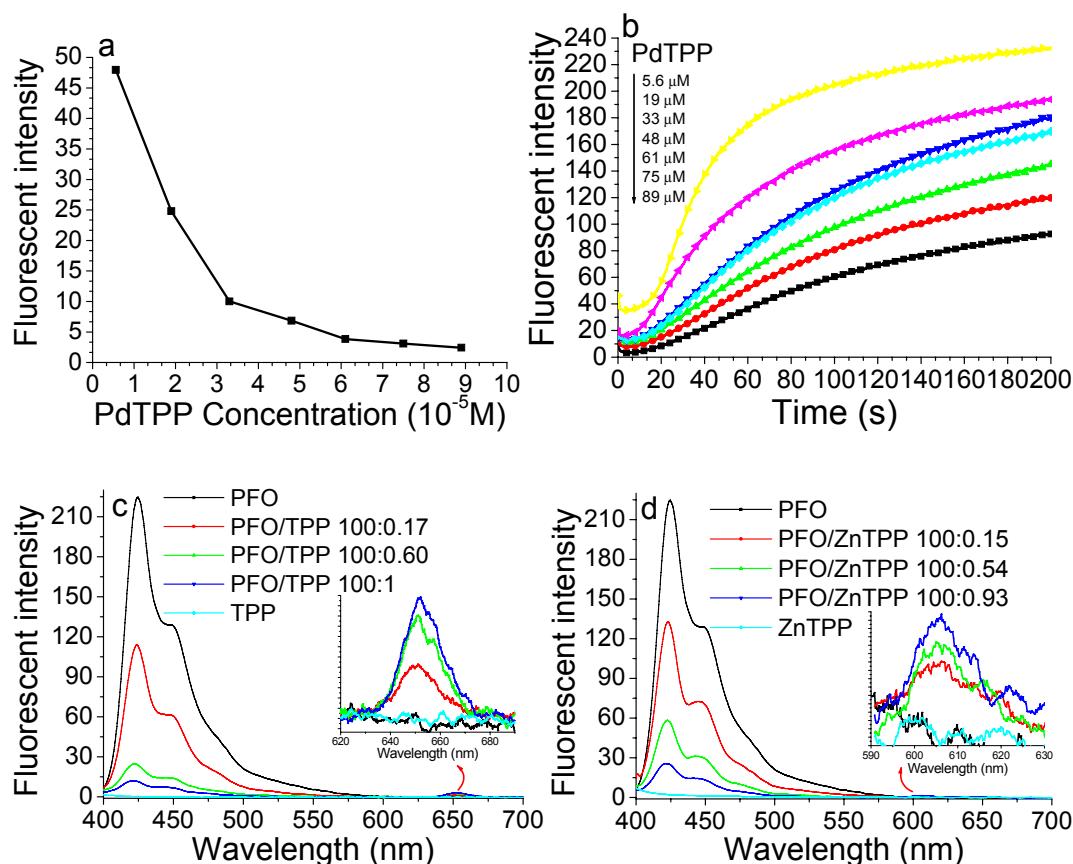


Figure S3. The fluorescent intensity (439nm) of PdTPP/PFO films (a) and their time-course fluorescent responses to saturate vapor of Benzylamine (b) at the different concentration of PdTPP. (PdTPP/PFO films spin-casted from their toluene solution: PFO, 3.8×10^{-3} M; PdTPP concentration varied from 5.6×10^{-6} M to 8.9×10^{-5} M). (c) The fluorescent spectra of PFO/TPP film upon the increasing of TPP concentration. (d) The fluorescent spectra of PFO/ZnTPP film upon the increasing of ZnTPP concentration. (Prim PFO, PFO/TPP and PFO/ZnTPP films spin-casted from their toluene solution: PFO, 3.4×10^{-3} M, TPP and ZnTPP concentrations were according to their different proportions as described. Prim TPP and

ZnTPP films spin-casted from their toluene solution, their concentrations were coincident with their max doping concentration as described.) the excitation wavelength was at 370 nm.

The film composition was optimized by investigating the fluorescent intensity (439nm) of PdTPP/PFO films and their time-course fluorescent responses to saturate vapor of Benzylamine (BA) as a function of PdTPP concentration. PdTPP/PFO films were spin-casted from their toluene solutions, 3.8×10^{-3} M of PFO was chosen as constant, the concentration of PdTPP varied from 5.6×10^{-6} M to 8.9×10^{-5} M. The fluorescent intensity (Figure a) and sensitivities to saturate vapor of BA (Figure b) were decreased by increasing the concentration of PdTPP. Fluorescence of PFO should be quenched efficiently by doping and recovered quickly after exposure, thus, 4.8×10^{-5} M of PdTPP was chosen since its efficient quenching and moderate sensitivity.

The fluorescence intensity of PFO was fully decreased along with the appearance of new bands of TPP (c) and ZnTPP (d) indicating energy transfer from PFO to Porphyrin system happened. the doped concentrations of TPP and MTPP were rather low and the composite films demonstrated low fluorescence quantum efficiency. Actually, no fluorescence new bands were found except for TPP/PFO and ZnTPP/PFO. In comparison between absorption of MTPP and emission of PFO, the fluorescence quenching of PFO/TPP and PFO/ MTPP system come from Föster energy transfer.

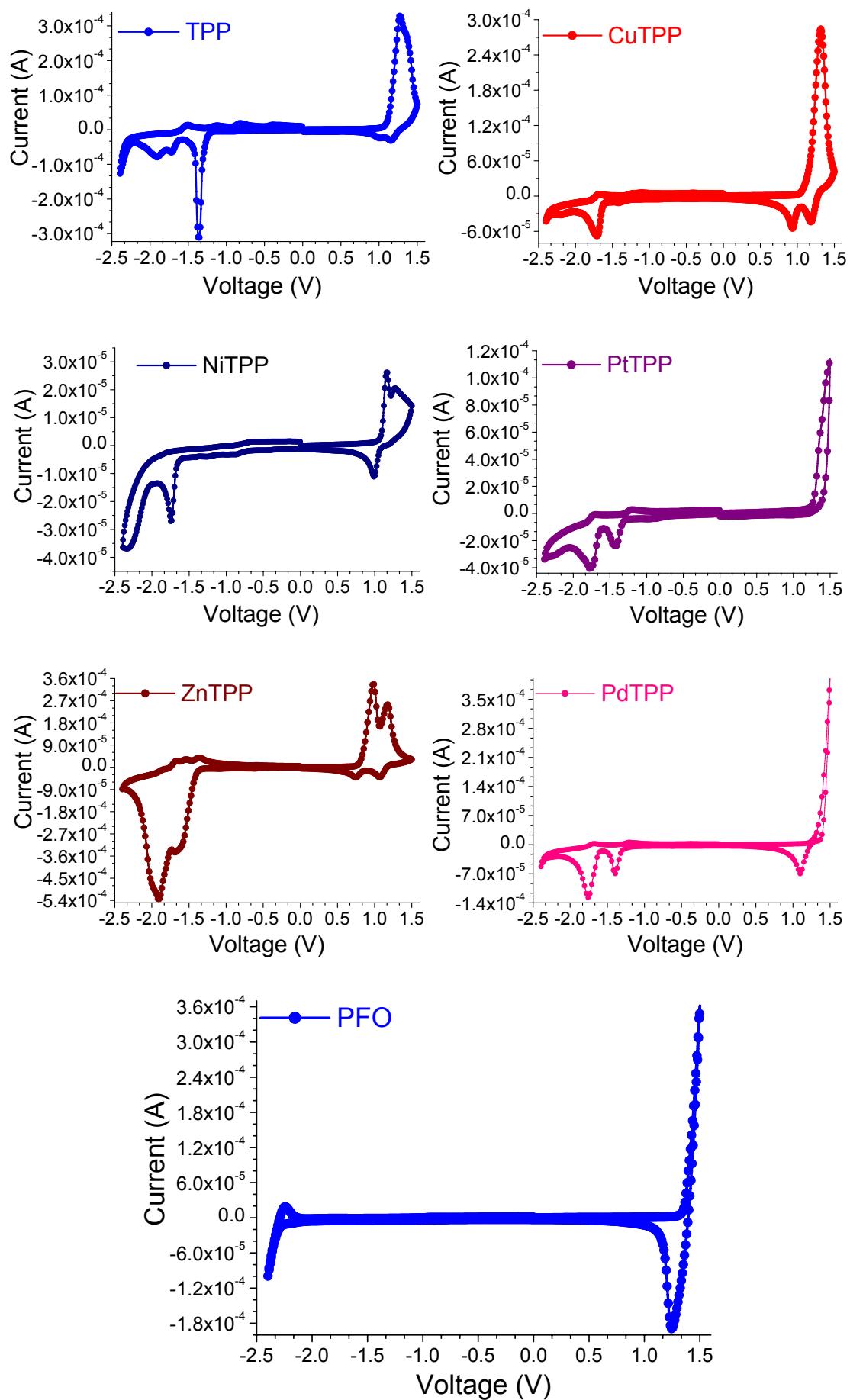


Figure S4. The CV curves of TPP, CuTPP, NiTPP, PtTPP, ZnTPP, PdTPP, and PFO on glassy carbon substrates at a sweep rate of 100 mV s⁻¹.

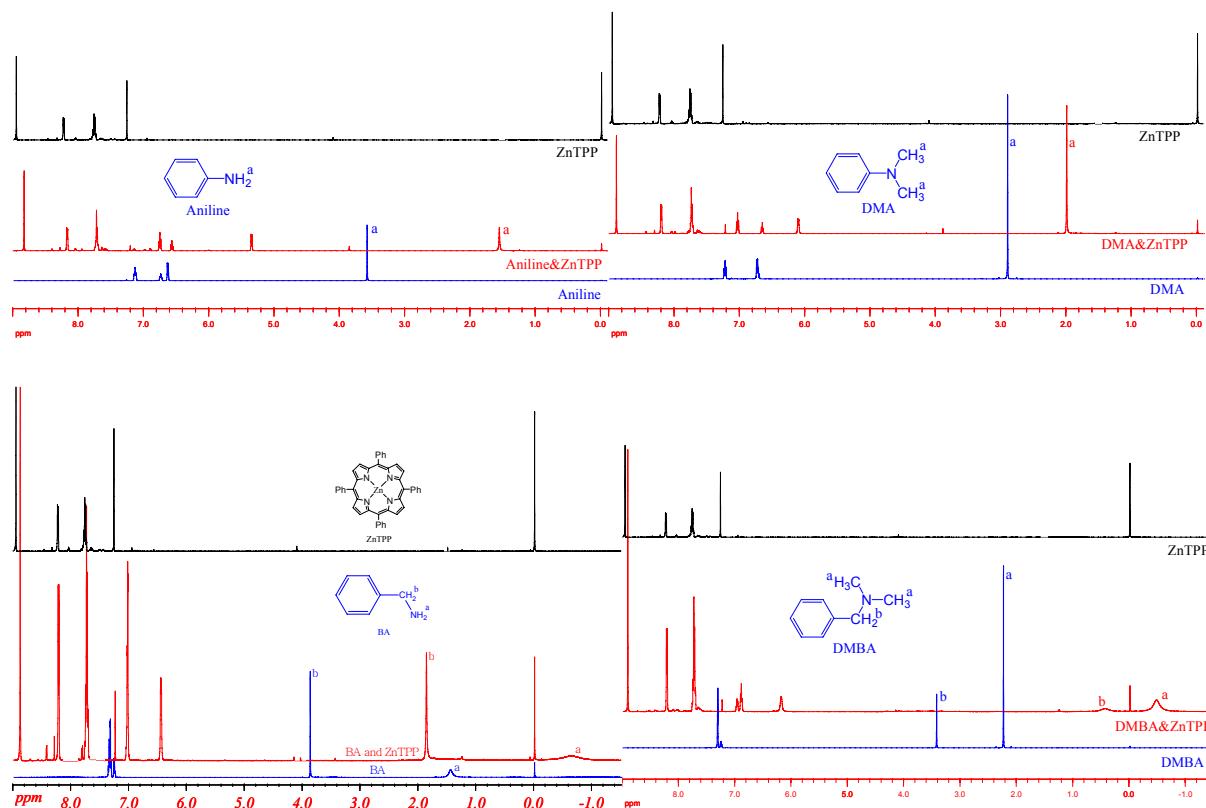


Figure S5. 1H NMR spectra of ZnTPP(black), amine(blue), ZnTPP&amine(red). Both of them were in chloroform-d solution, tetramethylsilane (TMS) was used as an internal standard.

¹H NMR spectra of each amine and ZnTPP was illustrated in supporting information as

Fig.S5. Here below shows ¹H NMR spectra of ZnTPP(black), amine(blue), ZnTPP&amine(red). ¹H NMR of all amines shifted to higher field in amine/ZnTPP indicating the existing of coordinating interaction between amine and ZnTPP. ^aH of aniline shifted 2.0 ppm, ^aH of DMA shifted 0.9 ppm, ^aH and ^bH of BA shifted 2.0 ppm, ^aH and ^bH of DMBA

shifted 3.0 ppm approximately after coordination with ZnTPP. It is clear that the shifted value of ¹H related with the electron intensity of porphyrin core and its chemical and/or structural environment in amines. For BA and DMBA, ^bH has similar chemical and structural environment in amines, thus, it was used for comparison. The shifted value of ^bH in DMBA was larger than that in BA, which indicates electron density of ZnTPP after coordination with DMBA was richer, and the shielding effect become stronger for ^bH. The different ¹H NMR shifted value of ^bH between BA/ZnTPP and DMBA/ZnTPP might arise from hydrogen bonding effect as described in the main text. This was in consistent with fluorescence recovery behavior of ZnTPP/PFO film upon exposure in BA and DMBA vapor.

For DMA and DMBA, ^aH has similar chemical and structural environment in amines, thus, it was used for comparison. the shifted value of ^aH in DMBA was larger than that in DMA indicating electron intensity of ZnTPP after coordination with DMBA was richer, and the shielding effect become stronger for ^aH. The different ¹H NMR shifted value of ^aH between DMA/ZnTPP and DMBA/ZnTPP might arise from substitute effect as described in the main text. Substitute effect (change from Phenyl to benzyl) resulting 0.9 ppm (DMA) to 3 ppm (DMBA) change and hydrogen bonding effect (change from methyl to hydrogen) resulting 3 ppm (DMBA) to 2 ppm (BA) change. This indicates that substitute effect plays more important role than hydrogen bonding effect for ZnTPP as described in film state.

It was surprised that the shifted value of ^aH at aniline and its fluorescence recovery behavior in solid state are different, this might arising from multiple effect such as the

differences of steric configuration, dynamic process, chemical environment between film state and solution state. The detailed studies will be conducted in the future.

Table S1. Vapor pressures of various analytes at 15°C (ppm).^a

	Aniline	DMA	BA	DMBA	Ammonia	Hydrazine
Vapor pressure	633	741	672	1879	7500000	15000
	CH ₂ Cl ₂	Acetone	Acetonitrile	Nitrobenzene	Ethanol	MAPA
Vapor pressure	577800	353780	86828	250	64696	148

^a The vapor pressure data are cited from CRC handbook of Chemistry and Physics, 90th Edition, CRC Press, 2010, VAPOR PRESSURE.

Table S2. Spectroscopic and electrochemical properties of TPP, MTPP, and PFO.

	Abs ^a , λ _{max} (nm)		PL ^a , λ _{max} (nm)		HOMO ^b	LUMO ^b	ΔE ^b	log ε _{max}	K _{sv}
	solution	film	solution	film	(eV)	(eV)	(eV)		(10 ⁶ M ⁻¹)
TPP	418	434	651 (low)	-	-5.84	-3.50	2.34	5.64	7.04
CuTPP	416	429	-	-	-5.81	-3.12	2.69	5.58	3.44
NiTPP	415	429	-	-	-5.80	-3.13	2.67	5.32	1.00
PtTPP	401	417	-	-	-6.00	-3.43	2.57	5.46	0.92
ZnTPP	423	432	596 (low)	-	-5.54	-3.36	2.18	5.67	4.14
PdTPP	417	431	-	-	-5.99	-3.46	2.53	5.48	2.14
PFO	386	394	416	423	-6.09	-2.46	3.63	4.58	-

^a The excitation wavelengths were at their maximum absorptions, and films were spin-casted from their toluene solutions on quartz plate.

^b HOMO= -|eE_{1/2}^{ox}+4.741ev|; LUMO= -|eE_{1/2}^{red}+4.741ev|; ΔE= HOMO-LUMO.

References

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