

Supporting Information:

Reaction of tetrachlorinated perylene bisimide in strong base to form asymmetric compound with charge transfer optical property

Wenqiang Zhang,^{a,b} Xuehong Zhou,^a Zengqi Xie,^{a,*} Bing Yang,^b Linlin Liu,^a Yuguang Ma^{a,*}

^a Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China.

Tel: +86-20-22236311; Fax: +86-20-87110606; E-mail: msxiez@scut.edu.cn; ygma@scut.edu.cn

^b State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China.

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1. Experimental details and synthesis.

Methods and materials. Solvents and reagents were purchased from commercial sources and were used as received, unless otherwise stated. For UV/vis and fluorescence measurements, spectroscopy grade solvents were used without further purification. Column chromatography was performed with silica gel (HaiYang Silica 60, particle size 0.035-0.070 mm). ^1H NMR, ^{13}C NMR, HMQC and HMBC spectra were recorded on a Bruker 300 MHz spectrometer operating at 300 and 75 MHz in deuterated chloroform solution at 298 K, using tetramethylsilane (TMS) or residual solvent peak as internal standard. High resolution mass spectrum was performed on the Pro-Orbital High Resolution LC-MC spectrophotometer. UV/vis spectrums were recorded with a Perkin-Elmer PE 950 under ambient conditions. Fluorescence emission spectra were recorded on a PTI QM4-2003 fluorescence spectrometer and were corrected against photomultiplier and lamp intensity. A long wavelength range mission corrected Hamamatsu photomultiplier R928 was used. Cyclic voltammetry (CV) measurement was performed on a CHI600D electrochemical workstation with a glass-carbon disk electrode as the working electrode, a Pt wire as the counter electrode, Ag/Ag^+ non-aqueous electrode as the reference electrode and TBAPF_6 (0.1 M) in CH_2Cl_2 / acetonitrile (positive) or DMF (negative) as electrolyte.

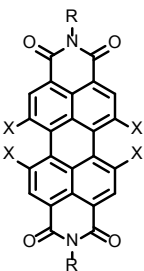
1.1 Synthesis of POI.

First of all, a portion of 390 mg (7.2 mol) was dissolved in 40mL DMF by sonication and 5 mL CH_3OH was added to improve the solubility of CH_3ONa in DMF. A portion of 300 mg (0.35 mmol) *N,N'*-bis(2,6-bisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisimide was added into one 100 mL flask, and treated with the solution of CH_3ONa under stirring, then stirred at room temperature for 12 hours. After that, the reaction mixture was poured into 150 mL glacial acetic acid under stirring, and diluted with 150 mL water subsequently. The product was extracted by dichloromethane (3×20 mL), and dried by sodium sulfate. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 /petroleum ether (50:50) as an eluent. After removal of the solvent with rotary evaporator, 30 mg (yield: 10%) of POI were obtained. ^1H NMR (300 MHz, CDCl_3 , ppm): δ = 8.65 (s, 1H), 8.61 (s, 1H), 7.99 (s, 1H), 7.96 (s, 1H), 7.34 (m,

6H), 6.57 (s, 1H), 4.09 (s, 3H), 3.20 (m, 1H), 2.98 (m, 1H), 2.76 (m, 2H), 1.40-0.75 (m, 24H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 171.58, 162.92, 147.95, 147.79, 147.59, 138.77, 135.27, 134.21, 134.00, 133.49, 133.40, 132.50, 131.94, 131.36, 130.37, 130.25, 129.73, 128.03, 124.90, 124.31, 124.13, 122.02, 119.57, 114.33, 112.02, 77.43, 77.01, 76.58, 54.14, 29.70, 29.18, 28.68, 28.30, 24.88, 24.56, 24.04, 23.48, 22.39, 14.23. HRMS (ESI, methanol): calculated for $\text{C}_{48}\text{H}_{41}\text{Cl}_4\text{N}_2\text{O}_4^-$ 849.1826 m/z, found, 849.1829. UV/vis (CH_2Cl_2): λ_{max} (ϵ_{max}) = 588 nm ($17500 \text{ M}^{-1} \text{ cm}^{-1}$). Fluorescence (CH_2Cl_2): λ_{max} = 609 nm, Φ_{FL} = 1%.

1.2 Effects of substituents on the reaction of POI formation.

Table S1. Effects of the steric hindrance of alkoxy anions and substituents at bay area and N-atom of PBI on the reaction of POI formation, respectively. All the reactions were conducted under room temperature.

PBI		X	R	Reaction condition	Result
	a	Cl		$\text{C}_2\text{H}_5\text{ONa}/\text{DMF}/\text{r.t.}$	Reacted
	b	Cl		<i>t</i> -BuOK/DMF/r.t.	No reaction
	c			$\text{CH}_3\text{ONa}/\text{DMF}/\text{r.t.}$	No reaction
	d	Cl	$\text{n-C}_4\text{H}_9-$	$\text{CH}_3\text{ONa}/\text{DMF}/\text{r.t.}$	No reaction

In order to investigate the effects of diverse substituents at different positions, several trial experiments were conducted. The increased size of the alkoxy substituents make it more difficult of nucleophilic reaction owing to the steric hindrance (Table S1 a and b). Addition of sodium ethoxide could make reactions occur, but potassium tert-butoxide (*t*-BuOK) led to almost no reaction occurring under the same reaction environment. In addition to the steric hindrance, the intrinsic characters of raw materials could also affect the reaction significantly. If the electron-withdrawing chlorine atoms were replaced by electron-donating phenoxy substituents (Table S1 c), the reaction did not occur. Interestingly, the substituents at N-atom could also affect the reaction. The special reaction proceeded quite easily for R=aryl, but more difficult for R=alkyl (Table S1 d).

2. Structure determination of the asymmetric POI.

2.1 ^1H NMR assignment of POI.

The ^1H NMR spectrum was assigned as shown in Figure S1. The structure of the POI was twisted and asymmetric. Herein, the asymmetric functional aryl phenyl groups would have different shielding effects on the different protons of the perylene core. Figure S1 showed the ^1H NMR (aromatic region) of POI in CDCl_3 at room temperature. As can be seen, in the low field region (8.8-7.8 ppm in Figure S1) there were four signals, which corresponded to the four protons on the perylene core (H^a , H^b , H^c , H^d). The totally different chemical environments for the four protons confirm the distortion of the perylene core into an unsymmetrical configuration owing to the exist of the N-O hexatomic ring in one side of the core. The carbon atom (connected with H^e) was a chiral center with four different functional groups. In addition to the proton H^e , a methoxy group was also connected with the chiral carbon (H^f 4.09 ppm in Figure S1), and it was confirmed on the ^1H NMR spectrum. Beyond that, the chemical shifts of the four atoms H^h , H^g , H^i were totally different as a result of the different chemical environment, which caused different shielding effects (3.20-2.76 ppm in Figure S1).

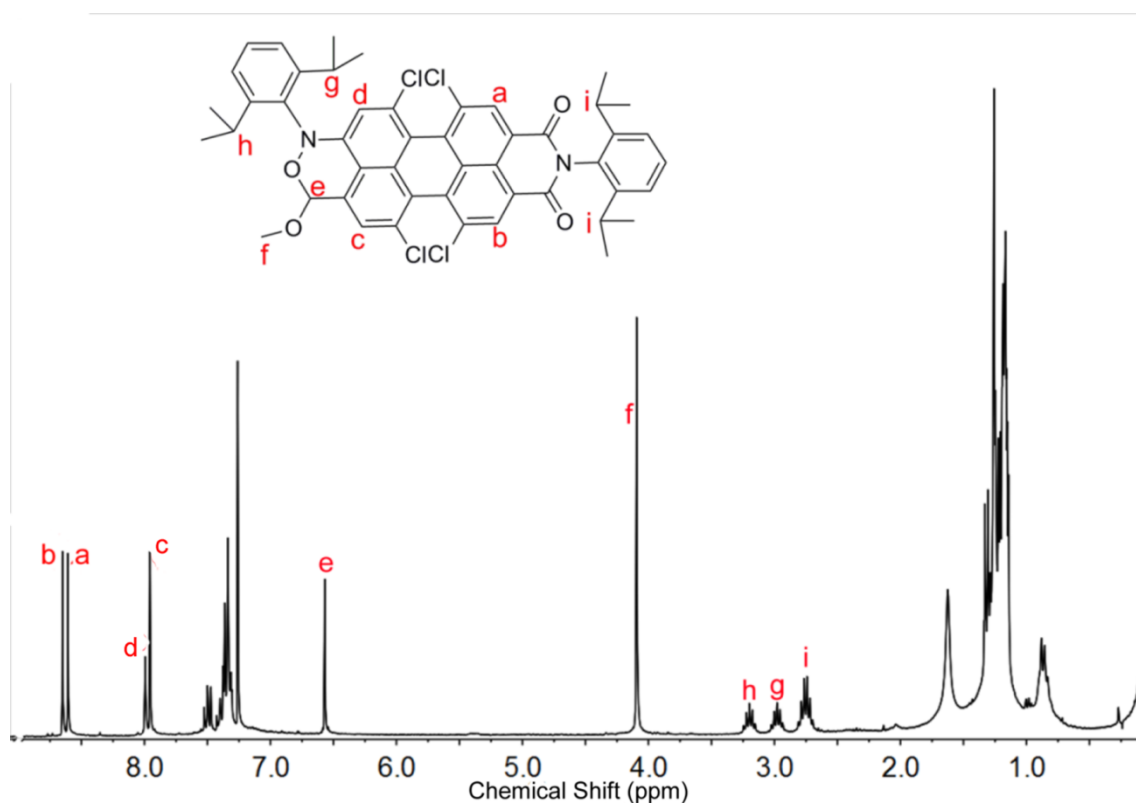


Figure S1. ^1H NMR spectrum of POI in CDCl_3 at ambient condition. The assignment of proton signals was made unambiguously.

2.2 HMQC spectrum of POI.

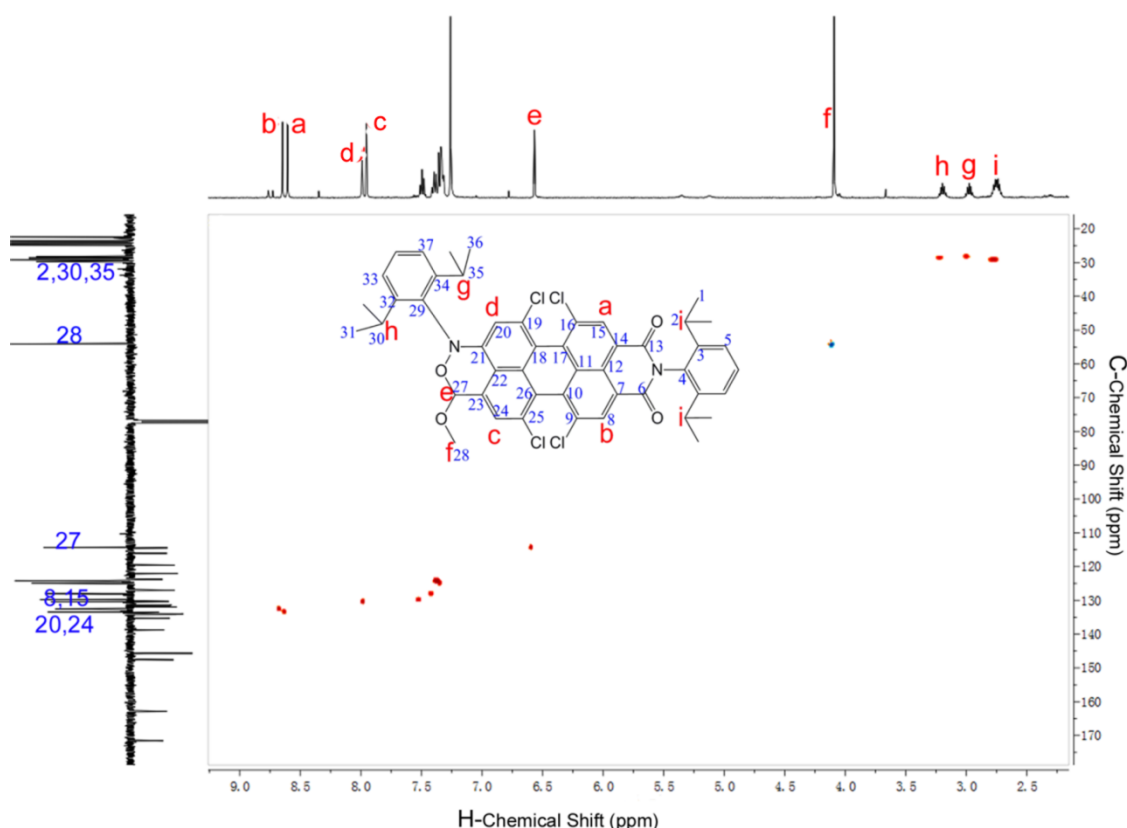


Figure S2. HMQC spectrum of POI.

2.3 HMBC spectrum of POI.

The spectrum of Heteronuclear Multiple Bond Correlation (HMBC) is one kind of two dimensional correlation spectra. It could illustrate the relation between carbon atoms and hydrogen atoms within the interval of two or three bond. In figure S3, some dominating correlation between C-H in spatial position was illustrated. The A area insert of spectra showed the relationship between H^b , H^a and several C atoms. The H^a was affected by the shield effect of C^{12} , C^{13} , C^{14} , C^{16} and C^{17} ; the H^b was affected by the shield effect of C^6 , C^7 , C^9 , C^{10} and C^{12} , as shown in the figure S3. However, the environment of H^c and H^d side was rather different: the N atom connected to the aromatic ring would not affect the environment of H^d as C atoms. So we could see the special signals in the left side of B area that indicating H^c be affected by the C^{27} atom, but no signals at H^d . The red C area showed the relation between H^e and C^{23} , C^{22} and C^{24} and more C atoms. The D and E areas illustrated the correlations between H^i and C^1 , C^3 , C^4 and C^5 , respectively. The cases of H^h and H^g

were as same as that of Hⁱ.

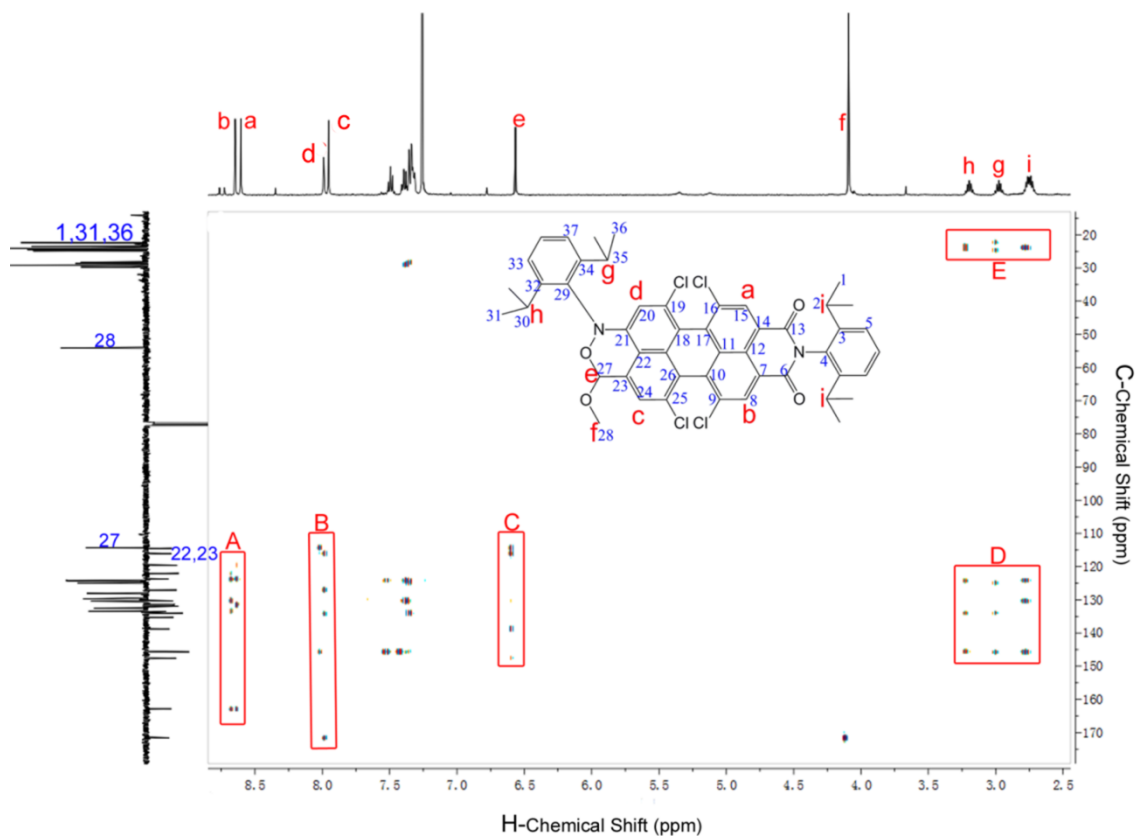


Figure S3. HMBC spectrum of POI.

2.4 NOESY spectrum of POI.

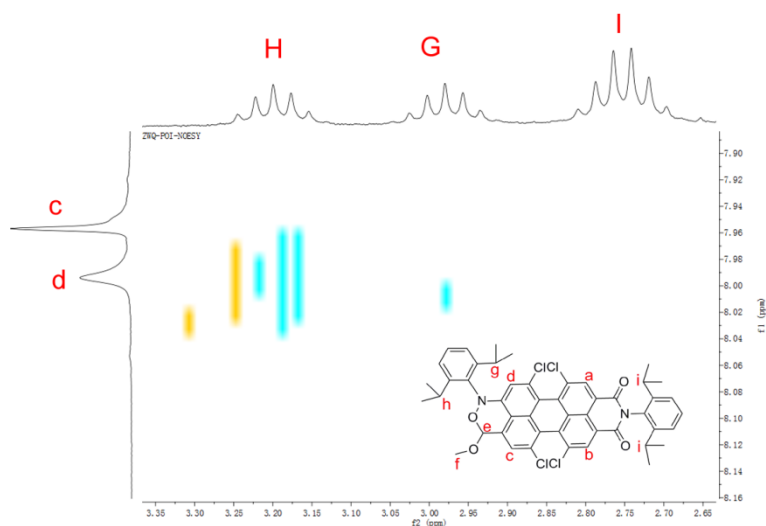


Figure S4. NOESY spectrum of the POI.

NOESY (Nuclear Overhauser Effect Spectroscopy) shows the relationship of protons within a

distance of 0.5 nm. In order to confirm the molecular structure, NOESY spectrum was conducted. The data shows the evidence of the asymmetric structure that the proton H and G both have related signals with proton H_d, but not related with proton H_c. Moreover, the signal intensity of relationship between proton H and H_d is much stronger than that between proton G and H_d. The phenomenon may be caused by the orientation of aryl group.

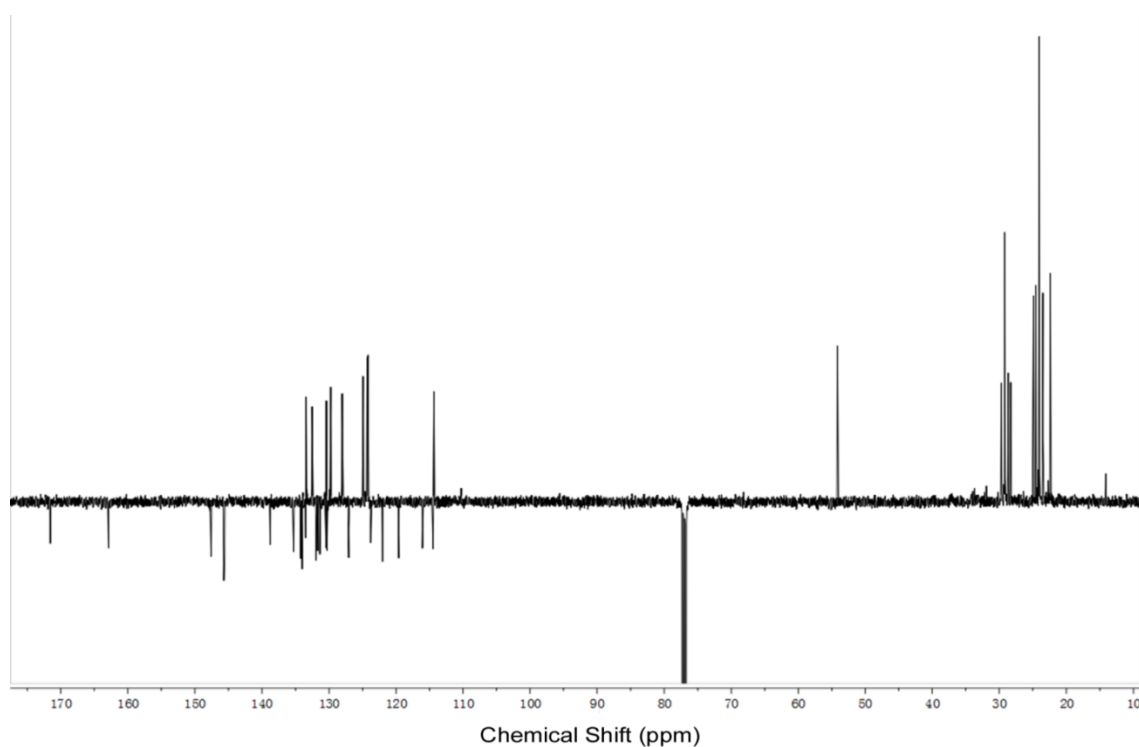


Figure S5. ¹³C NMR spectrum of POI.

2.3 FT-IR spectrum of PBI and POI.

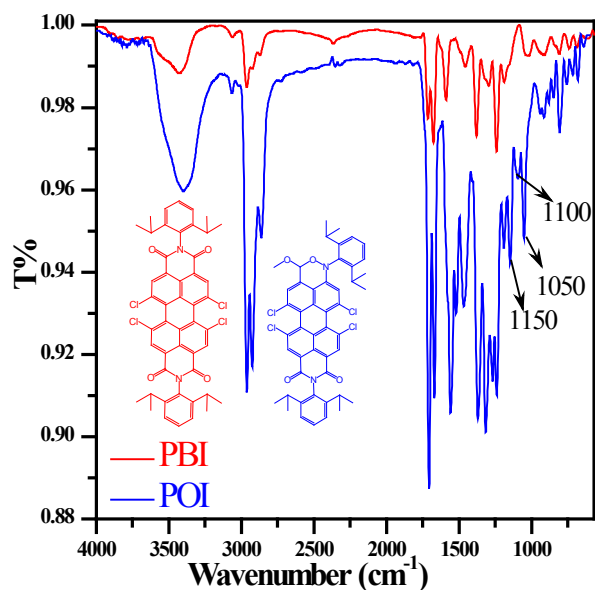


Figure S6. The FT-IR spectrum of the PBI and POI. The peak at 1150 cm^{-1} and 1050 cm^{-1} (blue line) was attributed to the C-O bond in the asymmetric derivative POI. Not observed in the compound PBI (red line).

3. Optical property of POI.

3.1 Solvatochromic effect of POI in various solvents and PL spectra of PBI and POI.

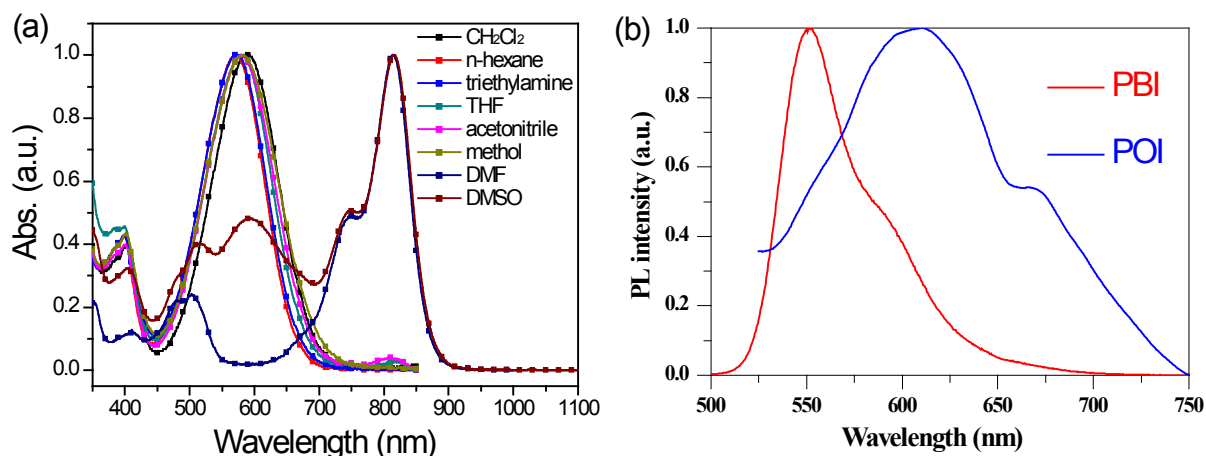


Figure S7. (a) The solvatochromic effect of POI in various solvents. (b) Normalized PL spectra of POI and PBI in dichloromethane solutions.

In low polar solvents like hexane the absorption showed a broad and structureless band in the region of 450-700 nm with full width of half maximum of 121 nm. With the increased polarity of the solvent the absorption is red-shifted but the shifts are not large when the high polar solvent is used,

e.g. the shift of the absorption maxima from hexane solution to dichloromethane solution is 17 nm (from 571 nm to 588 nm). Very special solvatochromic effect occurred in the strong polar solvents such as DMF and dimethyl sulfoxide (DMSO). According to the reported outcome before, in the presence of strong aprotic polar solvent, zwitterions might be formed with totally charge separation at ground state as shown in the inset of Figure 2 in the maintext.

3.2 UV spectrum of POI in CH_2Cl_2 solution and film.

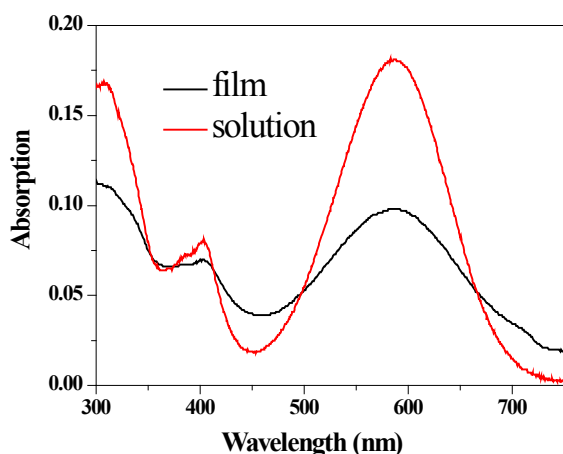


Figure S8. UV/Vis absorption spectrum of POI in CH_2Cl_2 solution and in film at room temperature. The film was spin-coating onto the quartz plate. The morphology of the film was uniform.

4. The electrochemical properties.

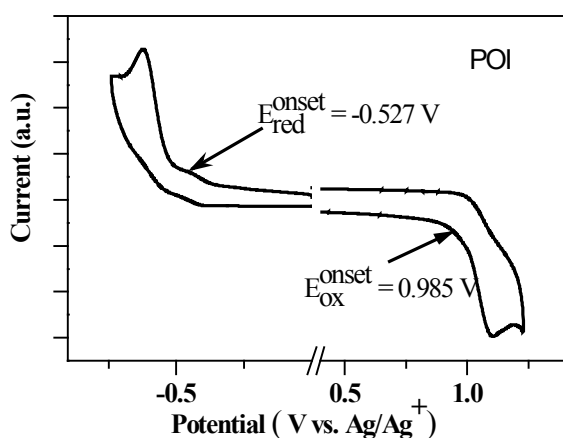


Figure S9. CV curves of POI. The HOMO/LUMO energy level and energy gap (E_g) were calculated by the onset potentials of the first oxidation/reduction peak in CV curve.

Table S2. Redox properties of POI (vs. Ag/Ag⁺).

$E_{\text{ox}}(\text{onset})$	$E_{\text{red}}(\text{onset})$	HOMO ^[a]	LUMO ^[b]	E_{g}^{CV}	$E_{\text{g}}^{\text{opt}[c]}$
(V)	(V)	(eV)	(eV)	(eV)	(eV)
0.985	-0.527	-5.39	-3.88	1.51	1.81

[a] HOMO energy level was calculated using the oxidation onset potential measured in CH₂Cl₂/acetonitrile (glass carbon electrode with 0.1 M TBAPF₆ as the supporting electrolyte). The voltage is referenced to an Ag/Ag⁺ standard.

[b] LUMO energy level was calculated using the reduction onset potential measured in DMF. The energy level of the ferrocene (Fc) reference (4.8 eV) was calibrated by measuring the cyclic voltammogram of Fc in corresponding solution.

[c] The optical band gap was calculated using the equation $E_{\text{g}}^{\text{opt}} = 1240 \times \lambda_{\text{edge}}^{-1}$, where λ_{edge} is the onset value of the absorption spectrum of the dichloromethane solution in the direction of longer wavelength.

An enhancement of the electron affinity of perylene bisimide by four chlorine substituents was observed by cyclic voltammetry of PBIs.^{S1} As known to all, the substituents at the positions of imide N atoms do not influence the energy levels of the compounds owing to the exist of nodes at the imide N atoms.^{S2} Two reversible reduction waves were detected at halfwave potentials of -0.87 V and -1.07 V vs. Fc/Fc⁺ (Fc: ferrocene) corresponding to the formation of radical anions and dianions. For comparison, perylene bisimides without bay substituents were reduced at around at -0.98 V and -1.2 V and oxidized at 1.2 V (vs. Fc/Fc⁺).

5. Reference:

- S1. a) J. Salbeck, H. Kunkely, H. Langhals, R. W. Saalfrank, J. Daub, *Chimia*. 1989, **43**, 6-9; b) Z. J. Chen, M. G. Debijs, Tony Debaerdemaeker, P. Osswald, and F. Würthner, *Chem. Phys. Chem.*, 2004, **5**, 137-140.
- S2. H. Langhals, S. Demmig, H. Huber, *Spectrochim. Acta, Part A*. 1988, **44**, 1189-1193.