

Electronic Supplementary Information for:

Surface Decorating of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Nanoparticles with the Chemically Absorbed Perylenetetracarboxylic Diimide

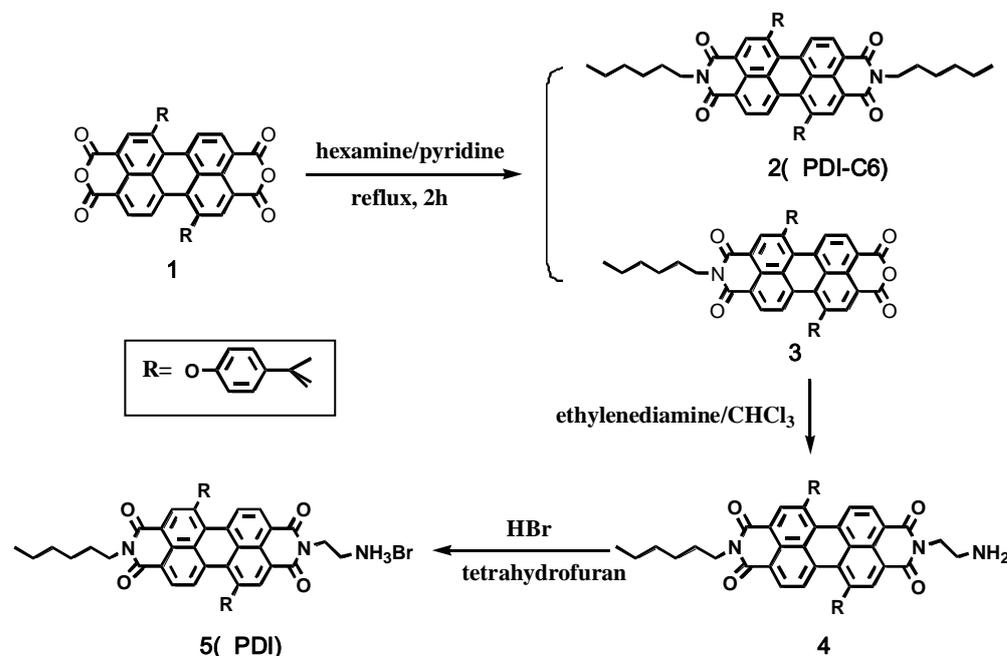
Ruimin Zhu^a, Chengguang Gao^a, Tingting Sun^a, Li Shen^b, Dejun Sun^{a,*}, Xiyou Li^{a,b,*}

a. Department of Chemistry, Shandong University, Jinan, Shandong, 250100, China;

b. College of Science, China University of Petroleum (East China), Qingdao, 266580, China

Email: xiyouli@sdu.edu.cn

1. Synthesis Details



Scheme 1. Synthesis process of PDI and PDI-C6.

N,N'-di-hexyl-1,7-di(*p*-tert-butylphenoxy)-3,4:9,10-tetracarboxylatediimide

(PDI-C6) 1,7-di(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic dianhydride (**1**) was synthesized according to the reported procedures.¹ Typically, a mixture of compound **1** and hexamine with mole ratio of 1:1 was dissolved in 70 ml pyridine and heated to reflux. The mixture was kept reflux for 2 h and then cooled to room temperature. The cooled reaction mixture was poured into 10% hydrochloric acid and stirred for one night. The resulted solid was separated from the solution by filtration and washed with water until neutral. The residue was dried under vacuum and purified by column chromatography on silica gel with chloroform as eluent. The second and third chromatographic band are **PDI-C6** (yield 30%) and compound **3** (yield 10%), respectively. Compound **3**: ¹HNMR (400Hz, CDCl_3 , TMS, PDI-C6): δ 0.88 (t, 6H), δ 1.32 (t, 4H),

δ 1.37 (s, 18H), δ 1.43 (t, 8H), δ 1.69 (t, 4H), δ 4.14 (t, 4H), δ 7.12 (d, 4H), δ 7.47 (d, 4H), δ 8.32 (s, 2H), δ 8.64 (d, 2H), δ 9.62 (d, 2H).

N-hexyl-N'-ethylamine -1,7-di(p-tert-butylphenoxyl)-

3,4:9,10-tetracarboxylatediimide (4) The solution of compound **3** in CHCl_3 was dropped into the solution of ethylenediamine (EA) in CHCl_3 (mole ratio of 3/EA=1/10) under nitrogen. The mixture was stirred for one night at room temperature. Compound **4** was obtained after the solvent was evaporated under vacuum and purified by column chromatography on silica gel with chloroform and methanol (9:1) as eluent.(yield 60%). This compound was not characterized; it was used as starting material directly in the next step.

N-hexyl-N'-ethylammonium bromide -1,7-di(p-tert-butylphenoxyl)-

3,4:9,10-tetracarboxylatediimide (PDI) Aqueous HBr (2 ml, 48%, Alfa) was dropped into the solution of compound **4** (0.047g) in tetrahydrofuran under nitrogen atmosphere at 60°C. The mixture was stirred for 4 h. **PDI** was obtained after the solvent was evaporated and recrystallized in methanol and diethyl ether. ^1H NMR (400Hz, CD_3OD , TMS): 0.99 (t, 6H), 1.32 (t, 2H), 1.41 (d, 18H), 1.67 (t, 2H), \square 4.07 (t, 2H), 4.46 (t, 2H), 7.16 (t, 4H), 7.57 (t, 4H), 7.99 (s, 1H), 8.07 (s, 1H), 8.42 (d, 1H), 8.52 (d, 1H), 9.41 (d, 1H), 9.46 (d, 1H).

PDI-P_{OA2}

The same procedure was followed to synthesize **PDI-P_{OA2}** as that of **PDI-P_{OA1}** except with octylammonium bromide (0.02 mmol) and PDI (0.04 mmol) instead.

PDI-P

The same procedure was followed to synthesize **PDI-P** as that of **PDI-P_{OA1}** except with PDI (0.06 mmol) and no octylammonium bromide.

2. Supporting figures and tables

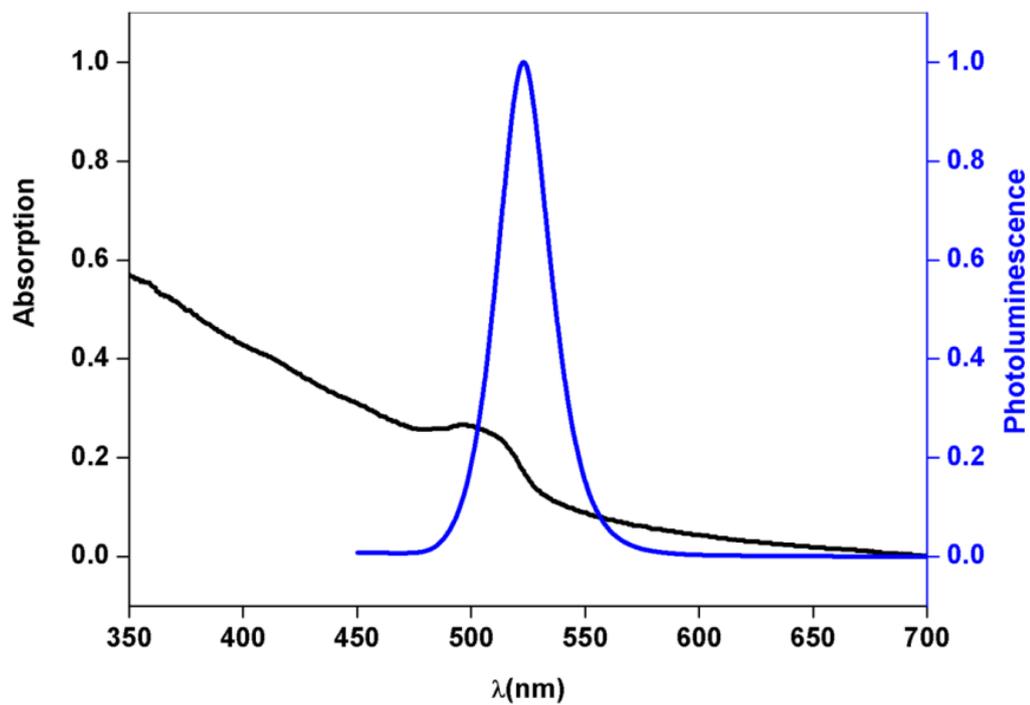


Figure S1. Absorption (black) and photoluminescence spectra (blue) of P_{OA}

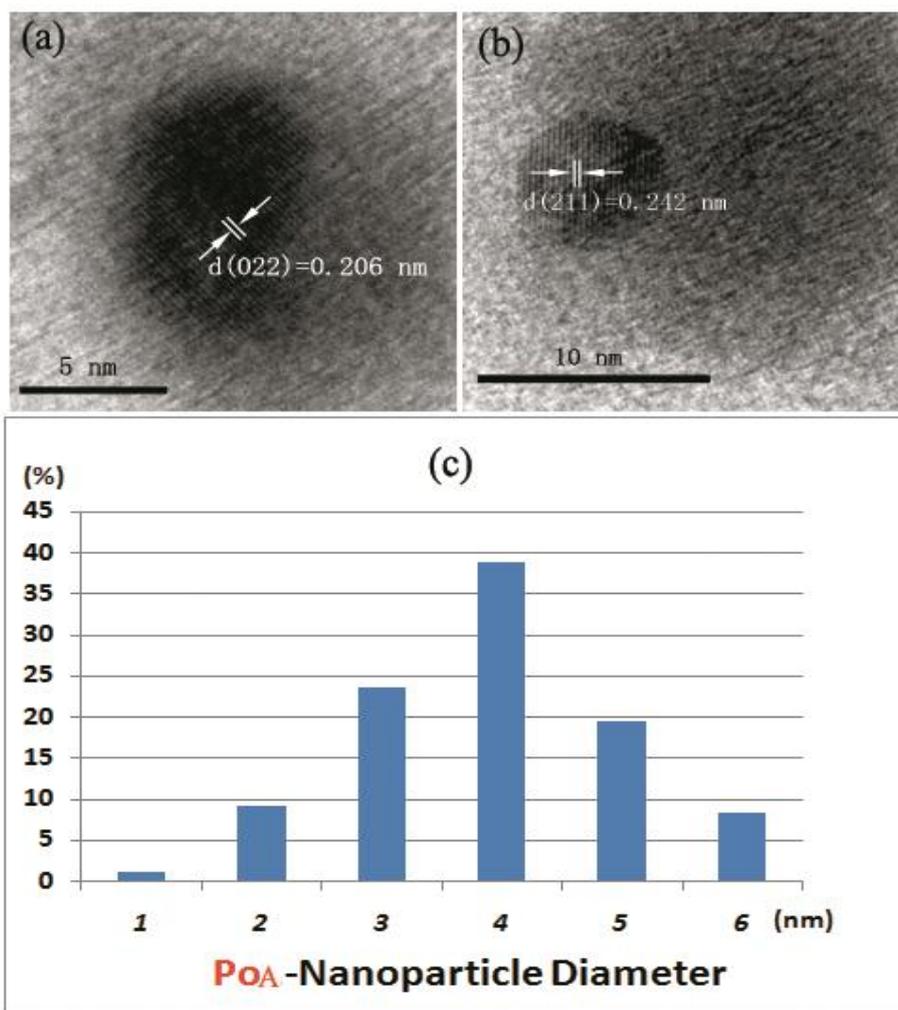


Figure S2. HRTEM images and size analysis of P_{OA} : (a, b) lattice fringe phase of P_{OA} (c) histogram of size dispersion of P_{OA} from 98 nanoparticles.

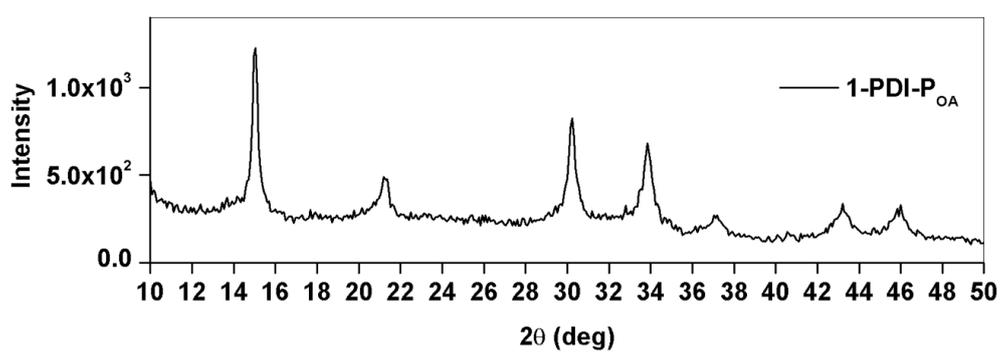


Figure S3. XRD pattern of $PDI-P_{OA2}$.

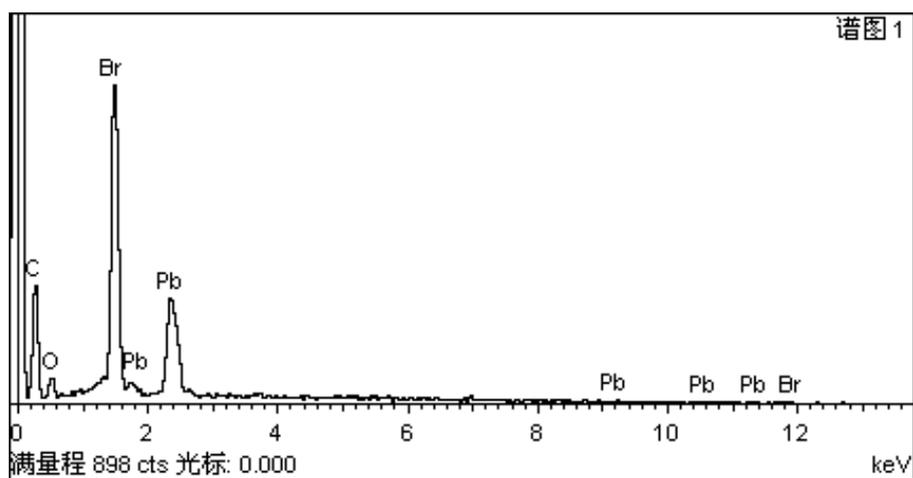


Figure S4: Energy dispersive spectrometer (EDS) of **PDI-POA1**. Atom number ratio of Pb: Br: O=1: 3.18: 1.8 means that PDI: $\text{CH}_3\text{NH}_3\text{PbBr}_3$ = 0.3: 1.

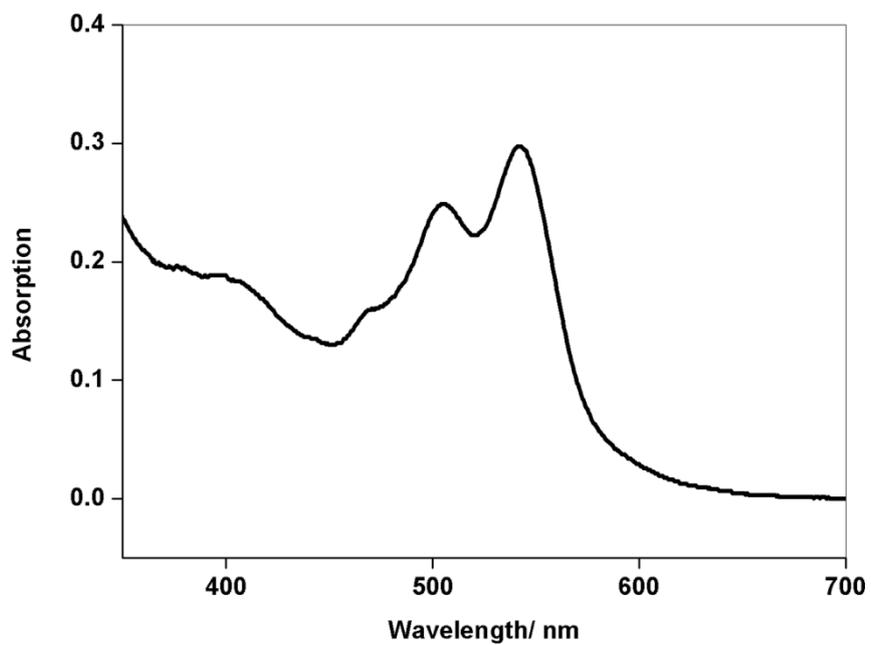


Figure S5: Absorption spectrum of **PDI-POA2** in toluene.

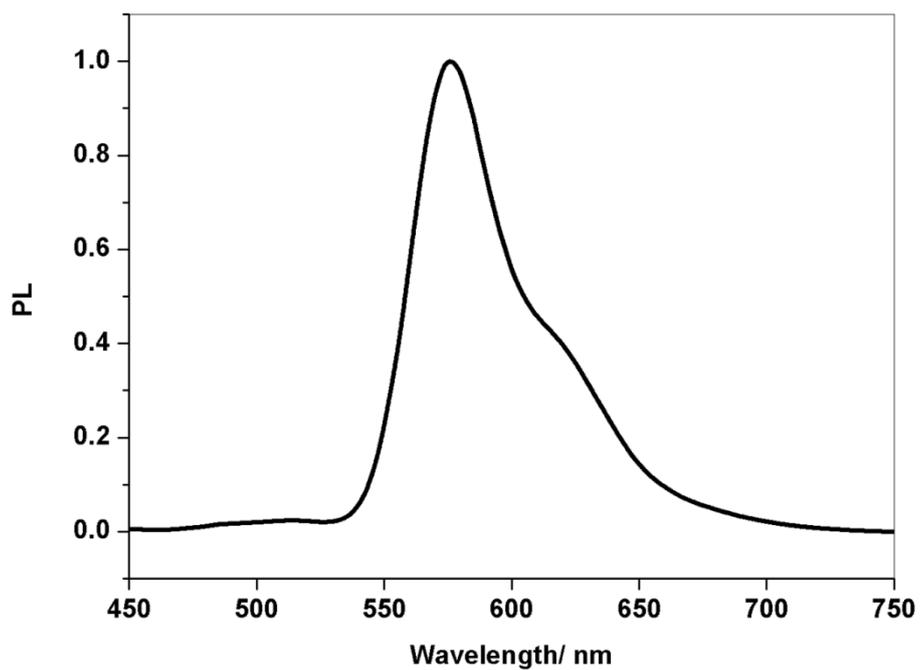


Figure S6: PL spectrum of **PDI-POA₂** in toluene.

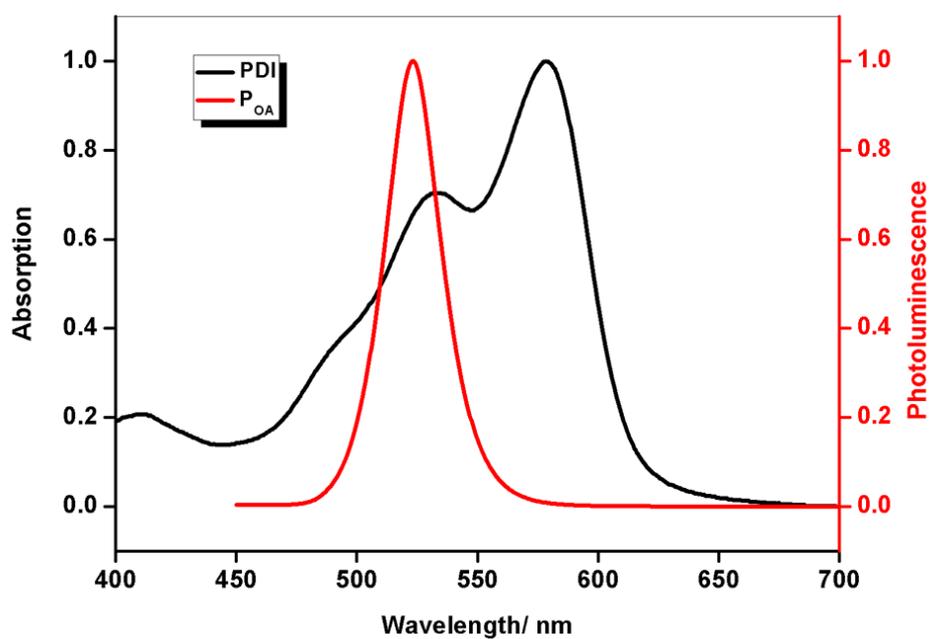


Figure S7. The overlap between the absorption spectrum of pure **PDI** (black) and the emission spectrum of **P_{OA}** (red).

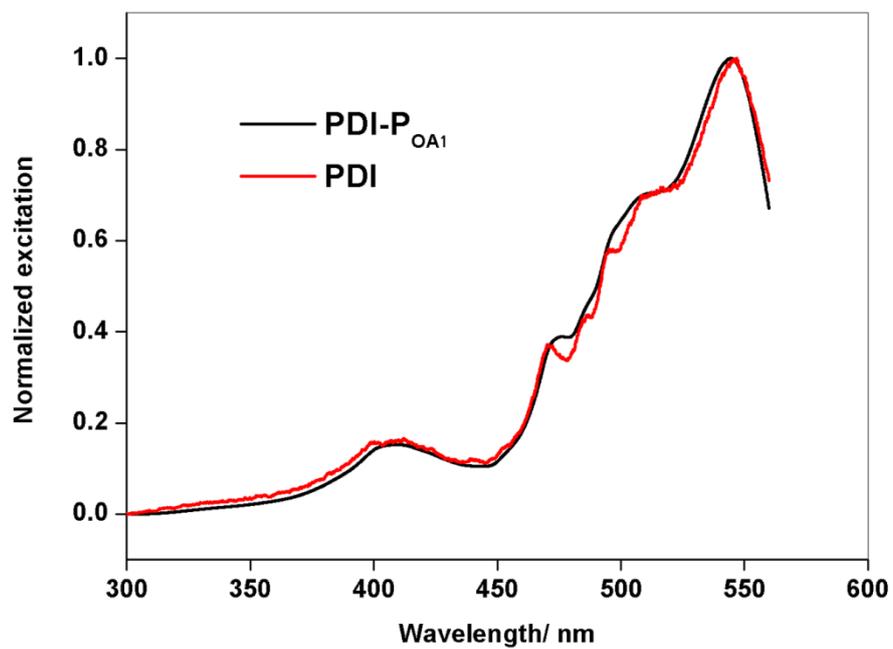


Figure S8. Excitation spectrum of **PDI-POA1** dispersion in toluene and PDI in DMF at the emission of 576 nm. This figure reveals no contribution from P_{OA} to the emission of PDI within **PDI-POA1**.

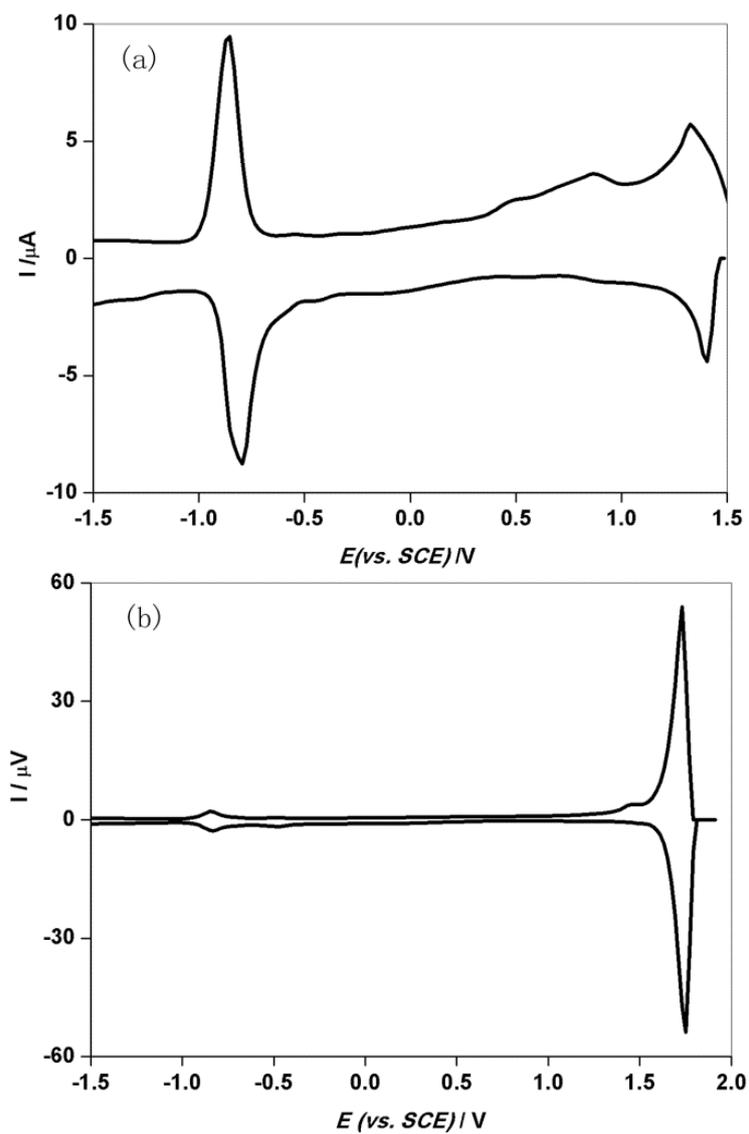


Figure S9. Differential pulse voltammetry (DPV) of **PDI**(a) and **PDI-C6**(b) in DMF with $(\text{nBu})_4\text{NPF}_6$ (0.1M) as a supporting electrolyte at a scan rate of 0.1 V/s. Palladium carbon electrode and Pt wire were used as working and counter electrodes.

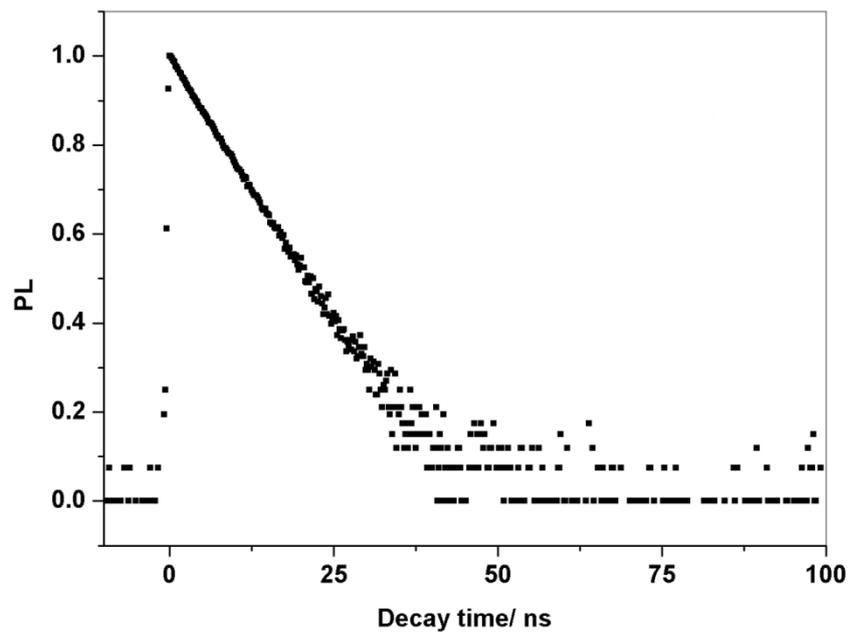


Figure S10. Time-resolved PL dynamics of **PDI-POA₂** in toluene probed at 523 nm after excitation at 370 nm.

Supporting references

1. J. Feng, Y. Zhang, C. Zhao, R. Li, W. Xu, X. Li, J. Jiang. *Chem. Eur. J.* 2008, 14, 7000.