

Supporting Information

Fast Charge Separation at Semiconductor Sensitizer-Molecular Relay

Interface Leads to Significantly Enhanced Solar Cell Performance

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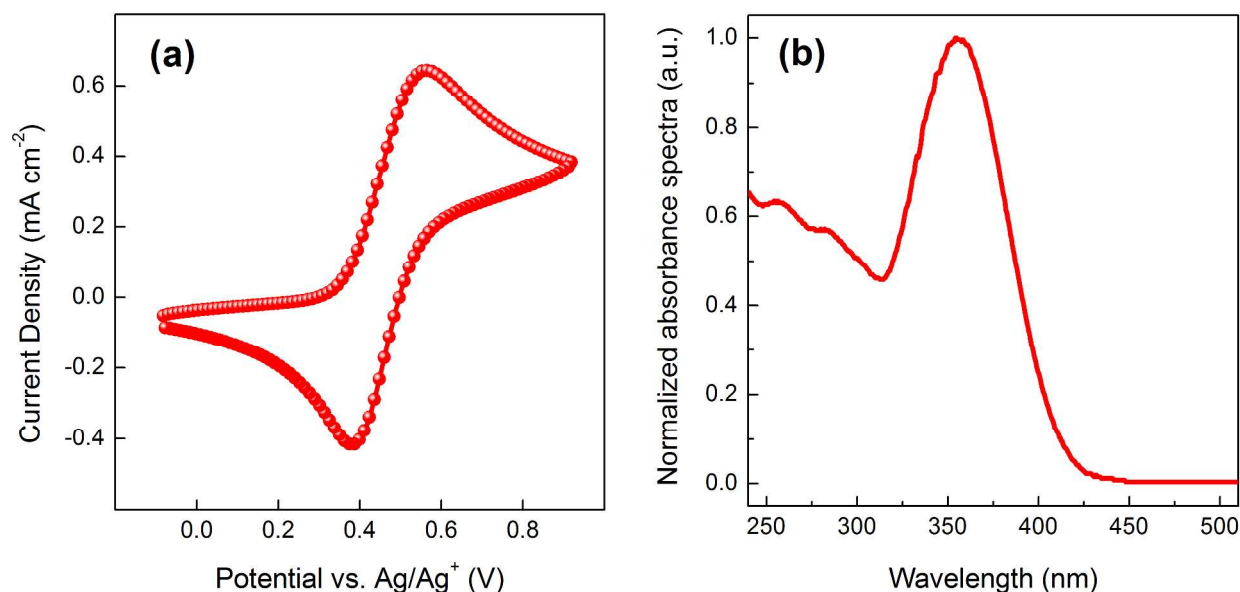


Figure S1. (a) Cyclic voltammogram of CdS/PAPC-sensitized TiO₂ photoanode in 0.10 M LiClO₄ acetonitrile solution. The reference electrode is Ag/AgNO₃, and the counter electrode is Pt wire. The scan rate is 100 mV s⁻¹; (b) absorbance spectrum of PAPC in acetonitrile.

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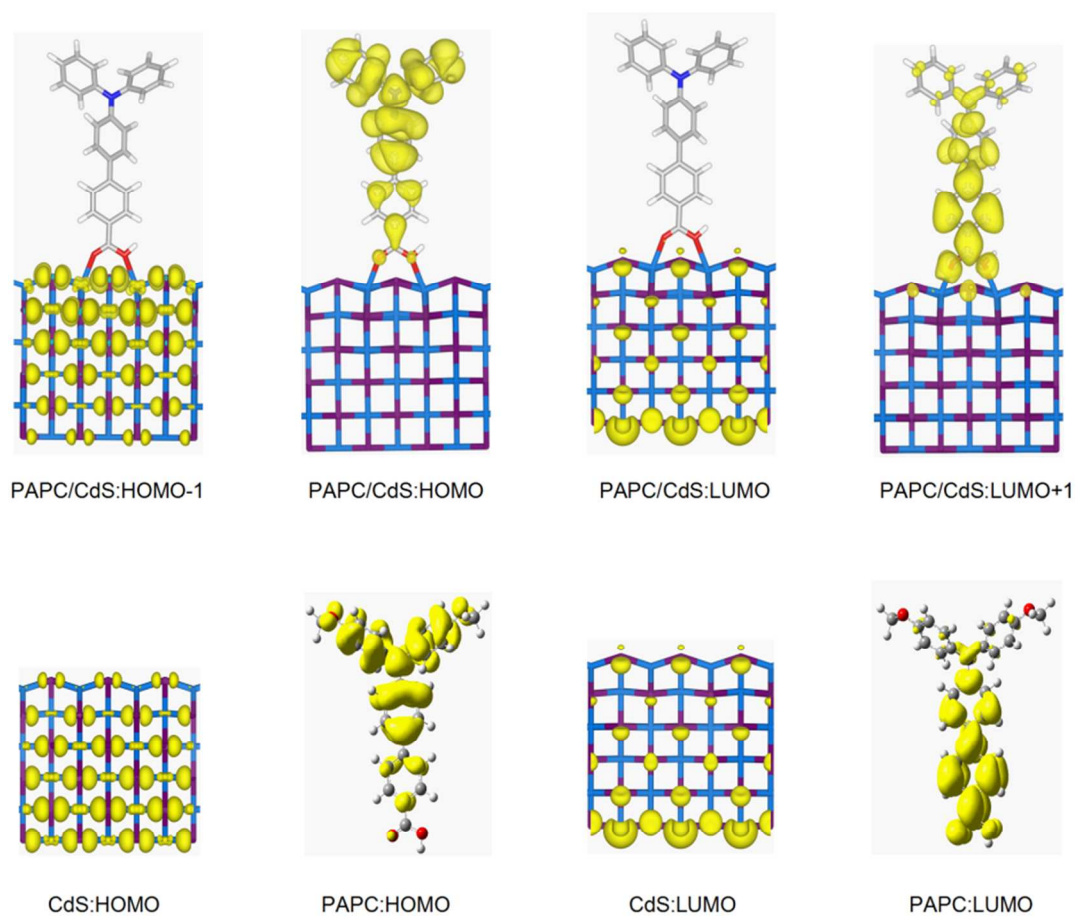


Figure S2. Γ -point frontier orbitals of CdS/PAPC, pure CdS, and isolate PAPC molecule system. PAPC is adsorbed on the (1 1 0) surface of CdS QDs.

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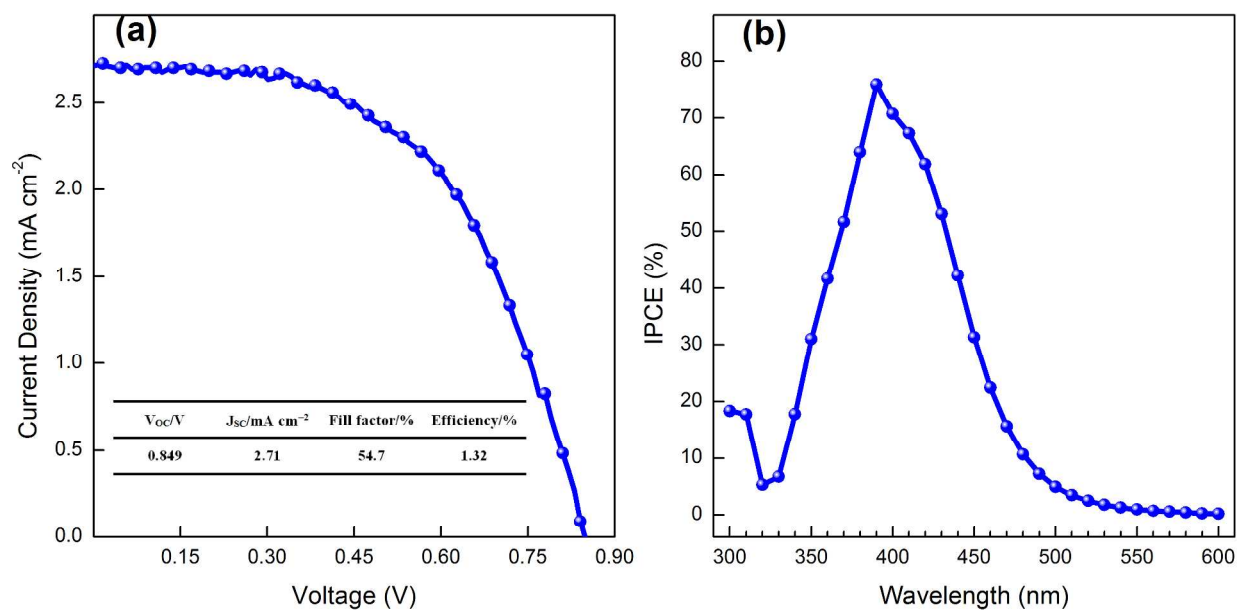


Figure S3. Photovoltaic performance of PAPC-sensitized TiO₂ solar cells: (a) photocurrent-voltage characteristics under AM 1.5G, 0.95 sun illumination; (b) IPCE spectra. The electrolyte consists of 0.20 M [Co(bpy)₃](PF₆)₂, 0.02 M [Co(bpy)₃](PF₆)₃, 0.50 M LiClO₄, and 0.50 M 4-tertbutylpyridine in acetonitrile solution. The counter electrode is platinized FTO glass. The active working area is 0.12 cm² determined by a mask.

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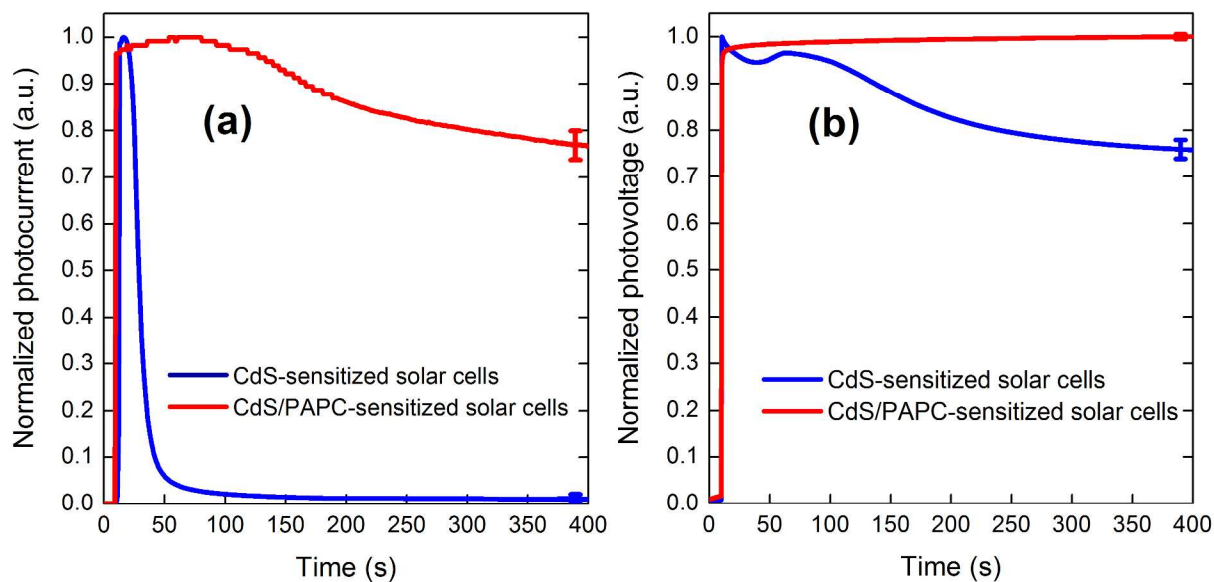


Figure S4. Photocurrent (a) and photovoltage (b) transient of CdS- and CdS/PAPC-sensitized solar cells under AM 1.5G illumination at 95 mW cm⁻².

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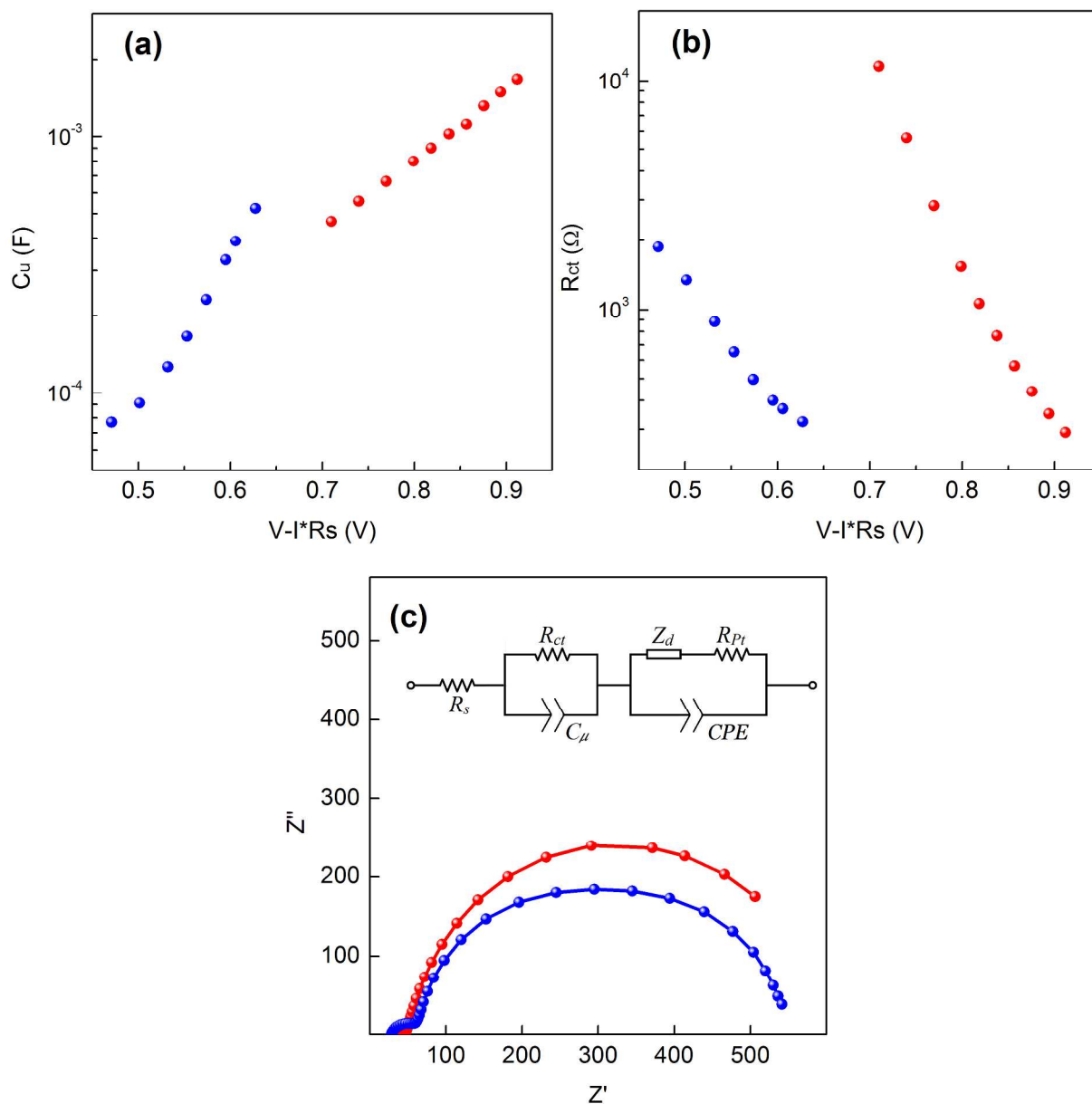


Figure S5. TiO_2 chemical capacitance (a) and interfacial charge transfer resistance (b) on different voltage for CdS- and CdS/PAPC- sensitized solar cells. (c) Typical EIS spectra for CdS-sensitized solar cells at 0.57 V (blue curve) and CdS/PAPC-sensitized solar cells at 0.86 V (red curve) respectively. The inset shows the equivalent circuit.

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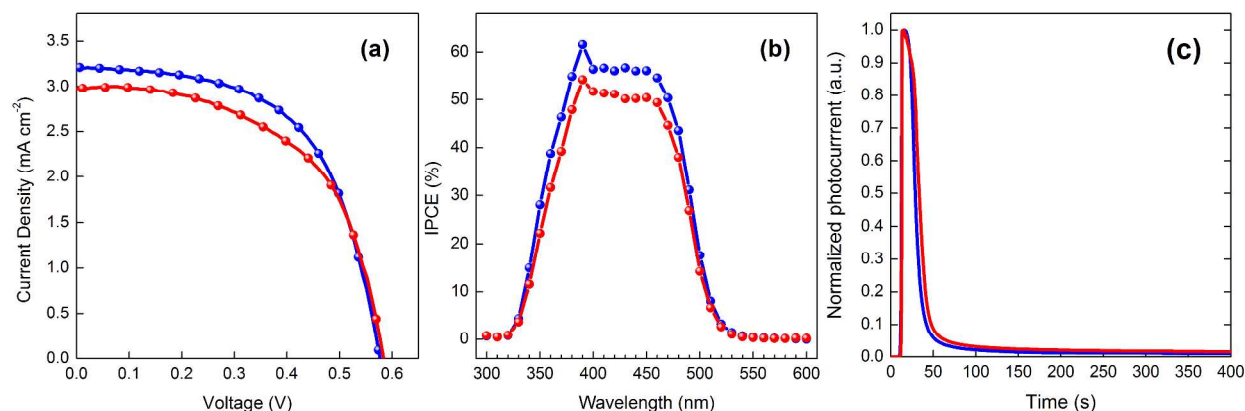


Figure S6. Photovoltaic and photostability performance of CdS (blue) and CdS/SA (red) - sensitized TiO₂ solar cells: (a) photocurrent-voltage characteristics; (b) IPCE spectra; (c) normalized photocurrent transient. The electrolyte consists of 0.20 M [Co(bpy)₃](PF₆)₂, 0.02 M [Co(bpy)₃](PF₆)₃, 0.50 M LiClO₄, and 0.50 M 4-tertbutylpyridine in acetonitrile solution. The counter electrode is platinized FTO glass. The active working area is 0.12 cm² determined by a mask.

Table S1. Characteristics of CdS and CdS/PAPC-sensitized TiO₂ solar cells under simulated AM 1.5G, 95 mW cm⁻² illumination.

Sample	V _{OC} /V	J _{SC} /mA cm ⁻²	Fill factor/%	Efficiency/%
CdS	0.576	3.21	58.1	1.13
CdS/SA	0.583	2.94	56.7	1.02

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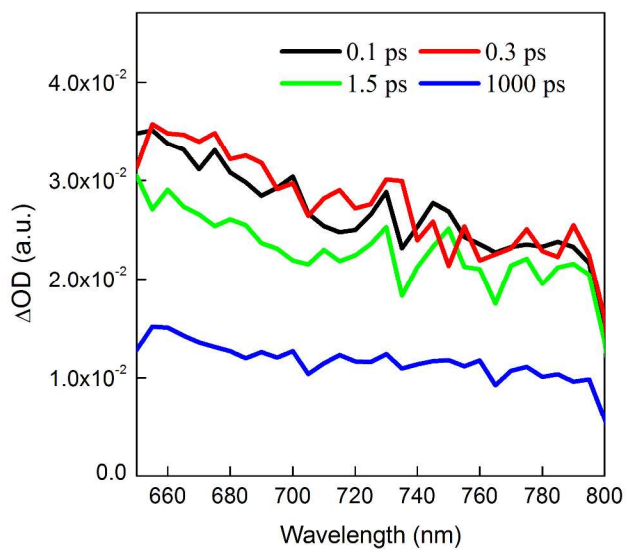


Figure S7. Transient absorption spectra during 0.1~1000 ps of a CdS -sensitized TiO₂ solar cell.

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Table S2. Photocurrent-voltage characteristics of the CdS- and CdS/PAPC-sensitized TiO₂ solar cells. The data of three typical devices are shown below and the best one is reported in manuscript for each condition.

Sample	V _{oc} /V	J _{sc} /mA cm ⁻²	Fill factor/%	Efficiency/%
CdS	0.576	3.21	58.1	1.13
	0.567	3.07	57.6	1.05
	0.583	3.18	56.7	1.11
CdS/PAPC	0.858	4.91	64.0	2.84
	0.855	4.78	64.5	2.78
	0.865	4.74	63.0	2.72

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Synthesis of 4'-(bis(4-(hexyloxy)phenyl)amino)biphenyl-4-carboxylic acid (PAPC)

Synthesis of 4-Bromobenzaldehyde

The reaction was carried out in a Teflon-lined stainless steel reactor (50 ml) coupled with a magnetic stirrer. 1-bromo-4-iodobenzene (1.41 g, 5.0 mmol), Pd/C catalyst (2.5 mol.%), PMHS (Si-H 15mmol), DBU (1.1 equiv.) and CH₃CN (10ml) were loaded into the reactor, which was charged with 1 MPa CO₂ and moved subsequently to an 80 °C oil bath controlled by a Haake-D3 temperature controller. After the reaction finished, the reactor was cooled down in ice water and the gas inside was carefully vented. The pure products were obtained via column chromatography separation (eluent: n-heptane/ethylactate=14:1), affording a compound of the 4-bromobenzaldehyde (0.47 g, 51%), ¹H NMR (CDCl₃, 400 MHz, ppm) δ7.69 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 9.98 (s, 1 H); ¹³C NMR (CDCl₃, 100 MHz, ppm) δ191.0 (C=O), 135.1(Ar), 132.4(Ar), 130.9(Ar), 129.7(Ar).

Synthesis of 2-(4'-formylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan

AcOK (1.47 g, 15 mmol), 4-bromobenzaldehyde (1.23 g, 6.67 mmol), PdCl₂(PPh₃)₂ (126 mg, 0.18 mmol), and pinacol (788 mg, 6.67 mmol) were added into dioxane (40 ml) and refluxed under Ar for 12 h. The mixture was then concentrated under reduced pressure. This solvent-addition/evaporation procedure was repeated thrice, which afforded pure 2-(4'-formylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, yielding 1.47 g, 95%. ¹H NMR (400 MHz, CDCl₃) δ: 10.05 (s, 1H, CHO); 7.96 (d, *J*=8.0 Hz, 2 H, H-Ar), and 7.86 (d, *J*=8.4 Hz, 2 H,

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H-Ar); 1.34 (s, 12H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 192.7 (C=O); 138.3 (Ar); 135.4(Ar), 128.9 (Ar); 84.5, 25.1 (CH₃).

Synthesis of 1-n-Hexyloxy-4-iodobenzene (1)

4-Iodophenol (2.0g, 9.0 mmol), 1-bromohexane (1.3 mL, 9.2 mmol), KOH (1.53 g, 26.8 mmol), and DMSO (20 ml) were placed in a one-neck 100 ml flask equipped with a reflux condenser. The mixture was kept stirring at 110 °C for 24 h. The resulting suspension was stirred for 30 min and was extracted four times with n-hexane. The organic mixture was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporation. The residue was purified by column chromatography with n-hexane as the eluent to afford compound hexyloxy-4-iodobenzene as a transparent oil (2.5 g, 91 %). ¹H NMR (CDCl₃, 400 MHz) δ 7.56-7.55(d, 2H, *J* = 8.80 Hz), 6.7-6.69 (d, 2H, *J* = 8.80 Hz), 3.94-3.92 (t, 2H, *J* = 6.40 Hz), 1.8-1.78 (m, 2H), 1.46-1.45 (m, 2H), 1.36-1.35(m, 4H), 0.93-0.91 (t, 3H, *J* = 6.80 Hz). ¹³C NMR (CDCl₃, 100MHz) δ 158.99, 138.1, 116.93, 82.38, 68.11, 31.54, 29.11, 25.66, 22.57, 14.01.

Synthesis of N,N-bis(4-hexyloxyphenyl)aniline (2)

Hexyloxy-4-iodobenzene (2.4 g, 7.9 mmol), aniline (2.98 g, 3.16 mmol), 1,10-phenanthroline (116 mg, 0.634 mmol), potassium hydroxide (0.7 g, 12.6 mmol), and cuprous chloride (32 mg, 0.316 mmol) were added into 30 ml toluene under N₂ at 100 °C, which was refluxed for 12 h before added 80 ml water. The crude product was extracted into dichloromethane and the organic layer was washed with water and dried over anhydrous sodium sulfate. After removing solvent

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under reduced pressure, the residue was purified by column chromatography with petroleum ether/DCM 9:1, obtaining the product of N,N-bis-(4-hexoxylphenyl)aniline as a pale yellow oil (1.15 g, 81%). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 7.22-7.18 (m, 2H), 7.09-7.08 (d, J = 8.80 Hz, 4H), 6.99-6.98 (d, J = 7.60 Hz, 2H) 6.91-6.84 (m, 5H), 3.98-3.95 (t, J = 6.40 Hz, 4H), 1.84-1.79 (m, 4H), 1.53-1.51 (m, 4H), 1.41-1.39 (m, 8H), 0.93-0.91 (t, J = 6.40 Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 155.23, 148.8, 140.92, 128.85, 126.37, 120.77, 120.37, 115.15, 68.18, 31.6, 29.32, 25.76, 22.61, 14.04.

Synthesis of 4-Bromo-N,N-bis(4-hexoxylphenyl)aniline (3)

NBS (281 mg, 1.67 mmol) was added into N,N-bis(4-hexoxylphenyl)aniline (0.742 g, 1.67 mmol) THF (10 ml) solution at 0 °C, which was then stirred for 2 h. The reaction was quenched by addition of water and extracted with DCM. The combined organic extract was dried over anhydrous MgSO_4 and filtered. Solvent removal by rotary evaporation followed by column chromatography over silica gel with petroleum ether/DCM =9:1 gave product of a pale yellow oil (0.85 g, 95%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.24-7.22 (d, 2H, J = 8.8 Hz), 7.05-7.0 (d, 4H, J = 8.6 Hz), 6.82-6.80 (m, 6H), 3.94-3.92 (t, 4H, J = 6.4 Hz), 1.84-1.77 (m, 4H), 1.51-1.44 (m, 4H), 1.35-1.33 (m, 8H), 0.93-0.91 (t, 6H, J = 6.0 Hz). ^{13}C NMR (100MHz, $[\text{D}_6]\text{acetone}$, ppm): δ 157.6, 151.0, 142.8, 130.8, 128.4, 122.4, 122.3, 117.2, 69.8, 33.4, 31.2, 27.6, 24.4, 15.4.

Synthesis of 4'-(bis(4-(hexyloxy)phenyl)amino)biphenyl-4-carbaldehyde (4)

4-bromo-N,N-bis(4-hexoxylphenyl)aniline (750mg, 1.68mmol), 4-(4,4,5,5-tetramethyl-1,3-

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dioxolan-2-yl)benzaldehyde (280mg, 1.2mmol), K_2CO_3 solution (2M), $Pd(PPh_3)_4(0)$ (60mg) and 40ml of DMF were stirred under argon at 100°C for 12h. The crude product was extracted into dichloromethane, and the organic layer was washed with water and then dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/dichloromethane and then methanol) on silica gel obtaining a white powder product (0.54 g, 82% yield). 1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.03 (s, 1H), 7.93-7.91 (d, 2H, $J = 8.4$ Hz), 7.73-7.71 (d, 2H, $J = 7.6$ Hz), 7.49-7.47 (d, 2H, $J = 7.2$ Hz), 7.12-7.10 (m, 4H), 7.00-6.99 (d, 2H, $J = 6.0$ Hz), 6.88-6.86 (m, 4H), 3.96-3.94 (t, 4H, $J = 6.6$ Hz), 1.87-1.82 (m, 4H), 1.58-1.37 (m, 12H), 0.93-0.91 (t, 6H, $J = 6.4$ Hz). ESI MS: m/z calcd. for $C_{37}H_{43}NO_3$: 549.7; found: 549.3.

Synthesis of 4'-(bis(4-(hexyloxy)phenyl)amino)biphenyl-4-carboxylic acid (PAPC)

4'-(bis(4-(hexyloxy)phenyl)amino)biphenyl-4-carbaldehyde (1.0 g, 1.82 mmol) and 35% H_2O_2 (2.73 mmol) was added into 8% NaH_2PO_4 THF solution (pH=4.5). Then $NaClO_2$ (2.73 mmol) solution was added slowly at 0 °C. After 20 min stirring, Na_2SO_3 was added into the mixture. The crude product was extracted into dichloromethane, and the organic layer was washed with water and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (dichloromethane/methanol 50/1, v/v) on silica gel giving a white powder product (0.63 g, 62% yield). 1H NMR (400 MHz, $CDCl_3$, ppm): δ 12.90 (s, 1H), 7.97-7.95 (d, 2H, $J = 7.6$ Hz), 7.72-7.70 (d, 2H, $J = 8.0$ Hz), 7.58-7.56 (d, 2H, $J = 7.6$ Hz), 7.06-7.04 (m, 6H), 6.93-6.91 (d, 2H, $J = 8.8$ Hz), 6.83-6.81 (d, 2H, $J = 6.0$ Hz), 3.95-3.92 (t, 4H, $J = 6.0$ Hz), 1.70-1.68 (m, 4H), 1.41-1.30 (m, 12H), 0.90-0.88 (t, 6H, $J = 6.0$ Hz). ESI MS: m/z calcd. for $C_{37}H_{43}NO_4$: 565.7; found: 565.3.

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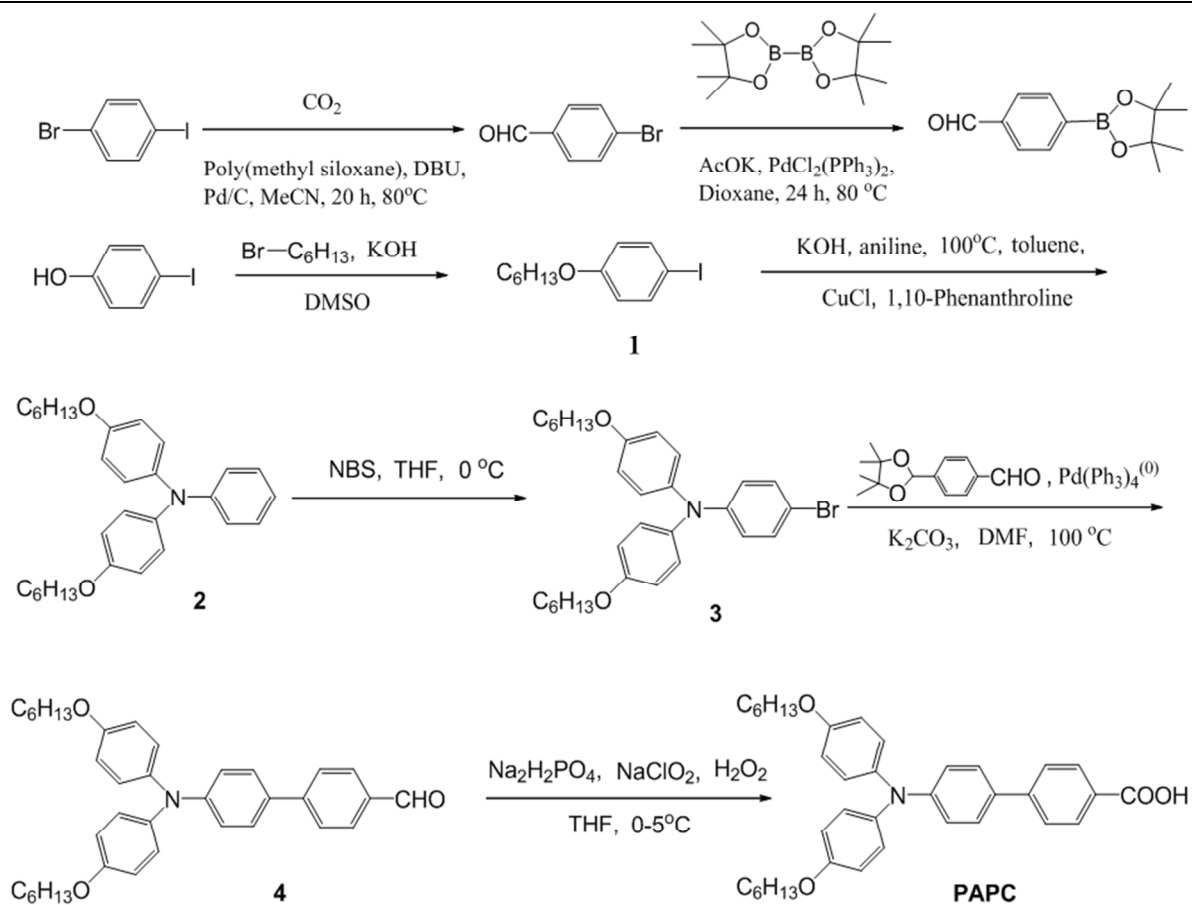


Figure S8. Synthetic route of 4'-(bis(4-(hexyloxy)phenyl)amino)biphenyl-4-carboxylic acid.