Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Combinatorial Synthesis of Soluble Conjugated Polymeric Nanoparticles and Tunable Multicolour Fluorescence Sensing

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Chemicals and Materials

2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (TCI, 99%), tetrakis(4-bromophenyl)ethane (HWRK Chem, 98%), 1,3,6,8-tetrabromopyrene (Sigma-Aldrich, 97%), tris(4-iodophenyl)amine (Aladdin, 98%), 1,4-phenylenebisboronic acid (Alfa, 96%), 3,4-dimethylthiophene (Energy, 98%), 3,4-ethoxylenedioxy thiophene (EDOT, Energy, 98%), 2-naphthaleneboronic acid (Energy, 98%), 9-anthraceneboronic acid (TCI, 98%), methyl 4-iodobenzoate (Energy, 98%), 4'-iodoacetophenone (Energy, 98%), 2,2,2-trifluoro-1-(4-iodo-phenyl)-ethanone (Ark pharm, 95%), pivalic acid (PivOH, TCI, 99%), tetrabutylammonium fluoride hydrate (Meryer, 98%), picric acid (PA, Xiya Reagent, 99.9%), tetrabutylammonium bromide (TBAB, Aladdin, 99%), palladium diacetate ($Pd(OAc)_2$, Sigma-Aldrich, 98%), potassium acetate (KOAc, Aladdin, 99%), and 1-methyl-2,4-dinitrobenzene (DNT, Xiya Reagent, 99.9%) were all used without further purification. Dimethyl acetamide (DMAc, 99.8%) was distilled with CaH_2 before use. Tetrakis(4-bromophenyl)methane was received as a gift from National Center for Nanoscience and Technology (China). 1,3,5-Triiodobenzene,[1] 1,3,5-tris(4-iodophenyl)benzene[2] and 3,4-bis(octyloxy)thiophene[3] were synthesized according to literature procedures.

Characterizations and measurements

High-Resolution Transmission Electron Microscopy (HR-TEM) images were obtained on a JEM-2100 microscope (JEOL, Japan) at an acceleration voltage of 200 kV. The Pd@SS-CNMs nanoreactor samples were prepared by drop-casting anhydrous ethanol dispersion on a carbon-coated 200 mesh copper grids. The SCPNs were dissolved in dried DCM (2 mg/ml) and drop-cast on ultrathin carbon copper grid carefully. The size of SCPNs on the copper grids were measured with Smile View software (JEOL, ver 2.1) and fitted with Gaussian model.

Nitrogen Adsorption/Desorption Isotherms were measured with an adsorption apparatus on an ASAP2010 instrument. The surface areas of the samples were calculated from the Brunauer–Emmett–Teller (BET) equation, and pore size distribution from the desorption branches of the isotherms were obtained through the Barrett–Joyner–Halanda (BJH) approach.

Inductively Coupled Plasma Atomic Emission Spectroscopy. The palladium content of nanoreactors was measured using a Thermo Elemental IRIS 1000 instrument.

Gel Permeation Chromatography (GPC). The number-averaged molecular weight (M_n) and the polydispersity index (PDI) of SCPNs were determined on a WATERS 1515 equipped with a series of PS gel columns, using THF as an eluent at 40 °C with a PS calibration.

Dynamic Light Scattering (DLS). The hydrodynamic diameters of the SCPNs were analyzed using a Zetasizer Nano ZS (Malvern, UK) at 25 °C with a 633 nm laser in tetrahydrofuran. The equilibrium time was fixed at 2 min and the concentration of SCPNs was changed from 5 mg/mL to 0.2 mg/mL to reach a stable result.

Nuclear Magnetic Resonance Spectroscopy. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR spectra (376 MHz) were obtained on a Bruker AVANCE FT NMR spectrometer in $CDCl_3$ equipped with a TXIZ probe (channels are ^1H, ^{13}C and ^{19}F).

Fluorescence Spectroscopy. Fluorescence spectra of SCPNs were recorded for quantitative analysis according to a previously described procedure[4, 5] using Fluorolog-3-P UV-VIS-NIR fluorescence spectrophotometer (Jobin Yvon, France). The Stern–Volmer quenching constant (K_{sv}) is obtained from the fitting of the plot of the relative

decrease of the peak intensity of SCPNs' fluorescence as a function of PA concentration. The Stern–Volmer equation in dilute solution is given as Equation (1).

$$\frac{I_0}{I} = 1 + K_{sv}Q \quad (1)$$

Where, I_0 and I are respectively the initial and final fluorescence intensity after addition of the analyte (PA), [Q] is the concentration of PA. Fluorescence-quenching titrations were carried out by placing 4 μg/ml solution of SCPNs (3 mL) in a quartz cuvette of 1 cm width. Then, a THF solution of PA (10 mM) was added in an incremental fashion (eg, 5μl per time) and mildly stirred with a microsyringe. For each addition, at least three fluorescence spectra were recorded repeatedly at 298 K to obtain a constant value. For SCPNs' film, polymeric films on a quartz plate (12 × 45 mm) were spin cast by a KW-4A Spin Coater (Chinese Academy of Sciences), using a spin rate of 2000 rpm from 1,2-dichlorobenzene solution of SCPNs, and placed under vacuum overnight before use. To generate a 20 nm film generally requires 50 μl 1,2-dichlorobenzene solution of SCPNs (0.5 mg/ml). For the SCPNs films, the angle between front films and exciting laser was fixed at 30 degree to avoid the influence from laser source, after exposure in a bottle containing saturated DNT vapor for different time, fluorescence spectra of the films were measured quickly.[6]

Fluorescence Quantum Yields (FQY) Measurements. Quinine sulfate (0.1 M H_2SO_4 as solvent, FQY=0.54) or fluorescein (0.1 M NaOH as solvent, FQY=0.84) was chosen as standards. The FQYs of SCPNs (in THF) were calculated according reference point method (Equation (2)).

$$\phi_x = \phi_{st}(I_x / I_{st})(\eta_x^2 / \eta_{st}^2)(A_{st} / A_x) \quad (2)$$

Where φ is the FQY, I is the measured integrated emission intensity, η is the refractive index of the solvent, and A is the optical density. The subscript "st" refers to standard with known FQY and "x" for the sample. In order to minimize reabsorption effects, absorption in the 10 mm fluorescence cuvette was kept below 0.08 at the excitation wavelength (360 nm or 440 nm).

Ellipsometric Measurement. SCPN films casted on silicon wafers were prepared according the aforementioned method. The film thickness was determined using W-VASE variable angle spectroscopic ellipsometer with Auto Retarder TM (J.A. Woollam Co., USA).

Calculation of the Limit of Detection (LOD) of PA. To determine the limit of detection (LOD) of $SCPN_{(32)}$ in THF solutions for PA, the PL quenching arising from analyte concentrations of the range 0–6 μM was evaluated. The LODs for PA in THF were determined using the 3σ IUPAC criteria ((Equation (2))) [7].

$$LOD = \frac{3\sigma}{\kappa} \quad (3)$$

Calculation of LOD for DNT vapor. According to the work of Sylvia et al.,[8] where the concentrations of DNT vapor was controlled based on Henry's law. We used a beaker containing 100 mL DNT aqueous solution (with different concentrations) and a headspace of 200 mL, and then the beaker was sealed with PE film and equilibrate for 2 days to provide the calculated 0-16 ppb DNT vapor in the headspace. After exposed in the headspace for 30 minutes, then $SCPN_{(33)}$ film was quickly taken out and measured with fluorophotometer. And the detection limit (~4 ppb) was acquired according to the method mentioned in the literature[5, 9]

UV−Vis−NIR Absorption Spectroscopy. Optical absorption spectra of dilute DMF solution of SCPNs were recorded in quartz cuvettes of 1 cm path-length employing Evolution 201 UV spectrophotometer (Thermo fisher, USA) at 25 °C. Ultraviolet absorption titration experiments with the addition of PA were carried in THF solutions.

Calculation of Band Gap of SCPNs.

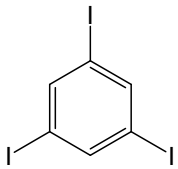
Kubelka–Munk function versus the energy of exciting light was used to evaluate band gap of SCPNs.[10]

Cyclic Voltammetry and HOMO and LUMO Energy Level of SCPNs.

The oxidation potentials and HOMO of SCPNs were determined by cyclic voltammetry (CV) in 0.1 M Bu_4NPF_6/CH_2Cl_2 solutions with a glassy carbon working electrode, a Pt sheet auxiliary electrode, and a saturated $Ag/AgNO_3$ reference electrode using a CHI660D electrochemical workstation (CH Instruments, Inc.). Ferrocene was used as an internal reference and the scan rate was set as 100 mV s^{-1}. The LUMO levels were elicited from the HOMO and band gap data.

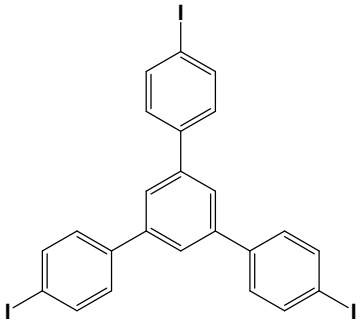
Synthesis of monomers

1, 3, 5-Triiodobenzene ($A_{(3)}$)[1]



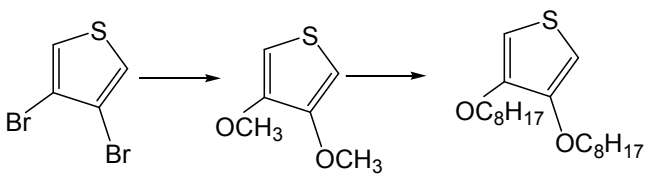
Ni powder (3.20 g, 54.5 mmol), I_2 (30.00 g, 118 mmol), and anhydrous DMF (75 ml) were charged into a 250 ml round-bottomed Schlenk flask. After evacuated at 0 °C for 15 min, the mixture was refluxed under N_2 at 187 °C for 8 h. Then the cooled solution was washed with 3 % aqueous HCl (150 ml) and CH_2Cl_2 (150 ml). The aqueous layer was extracted with CH_2Cl_2 (2 × 30 ml) again. The combined CH_2Cl_2 phase was washed with deionized water (3 × 100 ml) and dried over $MgSO_4$. The solvent was evaporated, and the residue was purified through column chromatography (silica, petroleum ether) to yield a white solid (4.30 g). The crude product was further subjected to another cycle of bromine-iodine exchange reaction. After worked-up and purified through column chromatography (silica, petroleum ether), a white solid was yielded, which was recrystallized twice from petroleum ether/THF to gain a white needle crystal (1.1 g, 17.3 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.01 (s).

1,3,5-Tris-(4-iodophenyl)benzene ($A_{(2)}$)[2]



1-(4-Iodophenyl)ethanone (3 g, 12.2 mmol) and p-toluenesulfonic acid (0.23 g, 1.34 mmol) was added into a 10 ml round-bottom flask and then stirred at temperature of 145 °C for 8 h. After cooled to room temperature, the crude product was purified with silica column chromatography (petroleum ether/ ethyl acetate=20/1) to obtain brown solid (1.3g, 48 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.40 (6 H), 7.68 (s, 3H), 7.81 (6 H).

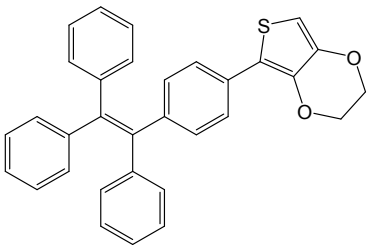
3, 4-Bis (octyloxy)thiophene($B_{(4)}$)[3]



Sodium methoxide (10.4 g, 0.19 mol) was added into a 250 mL schlenk flask which was fitted with a reflux condenser under nitrogen atmosphere. Methanol (80 mL) was added dropwise and stirred until sodium methoxide dissolved completely. 3,4-Dibromothiophene (2.5 g, 0.01 mol), KI (0.685 g, 0.0041 mol), and CuO (8.25 g, 0.104 mol) were added and then the mixture was refluxed at 97 °C for 48 h. After that, another port of sodium methoxide (10.4 g, 0.19 mol) was added carefully under an atmosphere of nitrogen. The mixture was refluxed for another 24 h. After most of the solvent was distilled out at the same temperature, the mixture was cooled, filtered, diluted with water, and extracted with ether. The organic layer was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator to afford yellow-brown oil. The crude product was purified by silica gel chromatography to give the product (0.28 g, 19.4 %). The above obtained 3,4-dimethoxythiophene (0.26 g, 1.39 mmol), 1-octanol (6.7 ml, 43 mmol), p-toluenesulfonic acid (27 mg, 0.156 mmol) and toluene (6 ml) were added in a 50 mL three-necked flask, then the mixture was refluxed for 24 h. After the mixture was cooled to room temperature, it was poured into 100 mL distilled water and extracted by hexane. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent by rotary evaporation, a colorless liquid was obtained. The crude product was purified using a silica gel column chromatography with petroleum ether/ethyl acetate (100 : 1, v/v) as eluent to give 3,4-bis(hexyloxy)thiophene as a white solid (0.4 g, 85 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.16 (s, 2H), 4.01–3.92 (t, 4H, J = 6.8 Hz), 1.87–1.74 (m, 4H), 1.48–1.24 (m, 20H), 0.88 (t, 6H, J = 6.8 Hz).

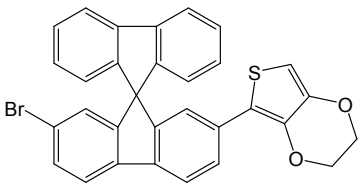
Synthesis of model compounds

Synthesis of $M_{(1)}$



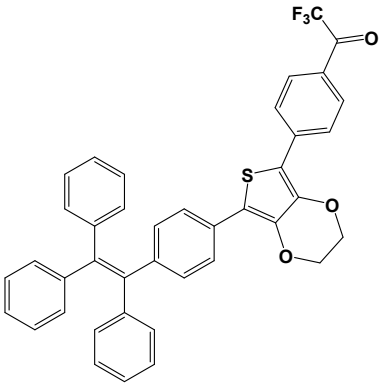
1-(4-Bromophenyl)-1,2,2-triphenylethylene (411 mg, 1.0 mmol), $Pd(PPh_3)_4$ (123 mg, 0.105 mmol) and K_2CO_3 (170 mg, 1.26 mmol) were successively added to a 10 ml sealed tube and DMAc (4 ml) was carefully dropped into the tube under nitrogen atmosphere. After two freeze-pump-thaw circles, the mixture was frozen by liquid nitrogen and EDOT (250 μL, 2.1 mmol) was injected with a microsyringe under nitrogen atmosphere. Then vacuum pumping and nitrogen filling were performed for three cycles, and finally the tube was sealed at atmosphere of nitrogen. The mixture was stirred at 80 °C for 10 h, cooled, diluted with DCM and washed with brine for three times. The collected organic layer was dried over anhydrous $MgSO_4$, filtered. After removal of the solvent by rotary evaporation, the crude product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (50 : 1, v/v) as eluent to obtain M_1 compound as a green solid (200 mg, 42 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.5 (d, 2H, J = 8.4 Hz), 7.01-7.18 (m, 18H), 4.24 (m, 4H). ^{13}CNMR ($CDCl_3$, 100 MHz) δ: 143.8, 143.7, 124.1, 141.9, 140.8, 140.51, 138.1, 131.6, 131.4, 131.3, 131.2, 127.7, 127.6, 126.3, 124.9, 117.4, 97.4, 64.6, 64.3. TOF-MS EI: for $C_{32}H_{24}O_2S^+$ calculated 472.1497, found 472.1499.

Synthesis of $M_{(2)}$



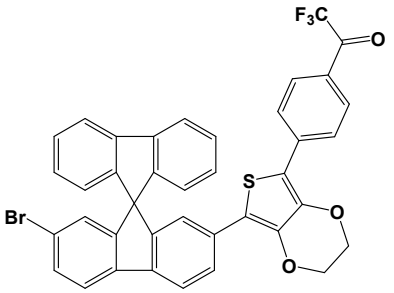
2,7-Dibromo-9,9'-spirobifluorene (502 mg, 1.06 mmol), $Pd(PPh_3)_4$ (123 mg, 0.106 mmol) and K_2CO_3 (170 mg,1.26 mmol) were successively added to a 10 ml sealed tube and DMAc (4 ml) was carefully dropped into the tube under nitrogen atmosphere. After two freeze-pump-thaw circles, the mixture was frozen by liquid nitrogen and EDOT (250 μL, 2.1 mmol) was injected with a microsyringe under nitrogen atmosphere. Then vacuum pumping and nitrogen filling were performed for three cycles, and finally the tube was sealed under nitrogen atmosphere. The mixture was stirred at 80 °C for 10 h and then cooled, diluted with DCM and washed with brine for three times. The collected organic layer was dried over anhydrous $MgSO_4$, filtered. After removal of the solvent by rotary evaporation, a brown solid was obtained. The crude product was purified with silica gel column chromatography with petroleum ether/ethyl acetate (20 : 1, v/v) as eluent to give M_2 compound as a white solid (85 mg, 15 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.86 (d, 2H, J = 7.6 Hz), 7.80 (s, 2H), 7.68 (d, 2H, J = 8.0 Hz), 7.47 (dd, 1H, J = 8.0 Hz, J=1.8 Hz), 7.39 (t, 2H, J = 8.0 Hz), 7.13 (t, 2H, J = 7.6 Hz), 6.97 (s, 1H), 6.8 (d, 1H, J=1.8 Hz), 6.76 (d, 2H, J = 7.6 Hz), 6.19 (s, 1H), 4.17 (m, 4H). ^{13}C NMR ($CDCl_3$, 100MHz) δ: 151.2, 148.8, 147.8, 142.1, 141.7, 140.3, 139.1, 138.1, 133.3, 130.8, 127.9, 127.1, 126.1, 124.1, 121.5, 121.2, 121.1, 120.2, 120.1, 117.3, 114.1. TOF-MS EI: for $C_{31}H_{19}BrO_2S^+$ calculated 534.0289, found 534.0294.

Synthesis of $M_{(3)}$



$M_{(1)}$ (100 mg, 0.212 mmol), 1-(4-bromophenyl)-2,2,2-trifluoroethanone (200 mg,1.484 mmol), $Pd(OAc)_2$ (1.5 mg, 0.006 mmol), KOAc (13.2 mg, 0.134 mmol), TBAB (18 mg, 0.056 mmol) were successively added to a 10 ml sealed tube and anhydrous DMAc (4 ml) was carefully dropped into the tube under nitrogen atmosphere. After three freeze-pump-thaw circles, the tube was sealed under nitrogen atmosphere. The mixture was stirred at 90 °C for 4 h and then cooled, diluted with DCM and washed with salt water for three times. The collected organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent by rotary evaporation, an orange solid was obtained. The crude product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (50 : 1, v/v) as eluent to obtain M_3 compound as a yellow solid (120 mg, 88 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.06 (d, 2H, J = 8.4 Hz), 7.87 (d, 2H, J = 8.4 Hz), 7.55 (d, 2H, J = 8.4 Hz), 7.01-7.21, (m, 17H), 4.36 (dd, 4H, J =16.0 Hz, J=5.0 Hz). ^{13}C NMR ($CDCl_3$, 100M Hz) δ: 179.5 (d), 143.7, 143.6, 143.0, 141.4, 141.4, 140.4, 140.2, 138.8, 131.8, 131.5, 131.4, 130.7, 130.34, 127.9, 127.8, 127.7, 126.9, 126.6, 125.6, 125.4, 119.2, 113.3, 64.8, 64.4. ^{19}F NMR ($CDCl_3$, 376 MHz)δ: -71.1 (s). TOF-MS EI: for $C_{40}H_{27}F_3O_3S^+$ calculated 644.1633, found 644.1635.

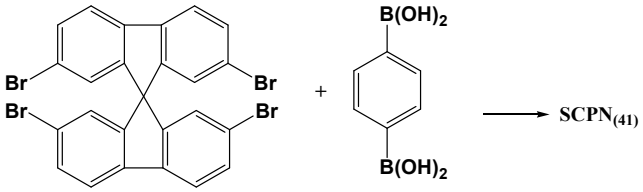
Synthesis of $M_{(4)}$



$M_{(2)}$ (60 mg, 0.112 mmol), 1-(4-bromophenyl)-2,2,2-trifluoroethanone (200 mg, 0.791 mmol), $Pd(OAc)_2$ (1.5 mg, 0.006 mmol), KOAc (13.2 mg, 0.134 mmol), TBAB (18 mg, 0.056 mmol) were successively added to a 10 ml sealed tube and anhydrous DMAc (4 ml) was carefully dropped into the tube under nitrogen atmosphere. After three freeze-pump-thaw circles, the tube was sealed under nitrogen atmosphere. The mixture was stirred at 90 °C for 4 h and cooled, diluted with DCM and washed with salt water for three times. The collected organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to give a dark brown solid. The crude product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (20 : 1, v/v) as eluent to obtain M_3 compound as a yellow solid (60 mg, 89 %). ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.99 (d, 2H, J = 8.0 Hz), 7.87 (dd, 3H, J =8.0 Hz, J=6.8 Hz), 7.81 (m, 3H), 7.69 (d, 2H, J = 8.0 Hz), 7.48 (dd, 1H, J = 8.0 Hz, J=1.8 Hz), 7.40 (td, 2H, J = 7.6 Hz, J=1.0 Hz), 7.14 (td, 2H, J = 7.6 Hz, J=1.0 Hz), 7.01 (d, 1H, J = 1.0 Hz), 6.81 (d, 1H, J = 1.8 Hz), 6.76 (d, 2H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100MHz) δ: 179.3, 151.3, 149.1, 147.7, 141.8, 141.3, 140.1, 140.0, 138.7, 132.4, 131.0, 130.6, 128.1, 128.1, 127.2, 126.9, 126.6, 125.5, 124.2, 121.7, 121.6, 121.4, 120.3, 120.2, 119.0, 114.1, 113.5, 65.9, 64.7, 64.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ: -71.1 (s). TOF-MS EI: for $C_{39}H_{22}BrF_3O_3S^+$ calculated 706.0425, found 706.0432.

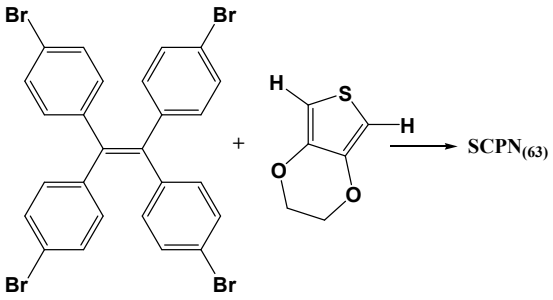
Preparation of SCPNs

Preparation of $SCPN_{(41)}$[1]



2,2',7,7'-tetrabromo-9,9'-spirobifluorene (94.8 mg, 0.15 mmol), Pd@SS-CNMs (10 mg, 1.5×10^{-3} mmol of Pd), p-phenylenediboronic acid (50 mg, 0.3 mmol) and tetrabutylammonium fluoride hydrate (663 mg, 2.1 mmol) were carefully added to a 10 ml sealed tube and dried at room temperature for 30 min. DMAc (2 ml) was dropped into the tube under nitrogen atmosphere. After three freeze-pump-thaw circles, the tube was sealed at atmosphere of nitrogen. The mixture was stirred at 100 °C for 120 h. After removal of the heterogeneous catalysts by centrifugation, the supernatant was concentrated and added dropwise into methanol (60 ml). The precipitate was isolated through centrifugation and washed with methanol and n-hexane for three times and then dried under vacuum overnight (38 mg, 55 %).

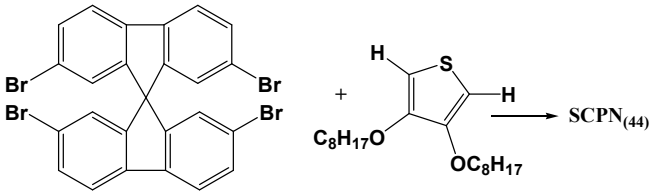
Preparation of $SCPN_{(63)}$:



Tetrakis(4-bromophenyl)ethene ($A_{(6)}$, 96.6 mg, 0.15 mmol), Pd@SS-CNMs (10 mg, 1.5×10^{-3} mmol of Pd) and tetrabutylammonium fluoride hydrate (663 mg, 2.1 mmol) were successively added to a 10 ml sealed tube and vacuum dried at room temperature for 30 min. Pivalic acid (10 μl, 0.13 mmol) and DMAc (2 ml) were carefully dropped into the tube under nitrogen atmosphere. After two freeze-pump-thaw circles, the mixture was frozen by liquid nitrogen and EDOT ($B_{(3)}$, 32 μL, 0.3 mmol) was injected with a microsyringe under nitrogen atmosphere, then several vacuum pumping and nitrogen filling cycles were conducted. Finally the tube was sealed in nitrogen atmosphere. The mixture was stirred at 110 °C for 120 h. After removal of the heterogeneous catalysts by centrifugation, the supernatant was concentrated and added dropwise into stirred methanol (60 ml). The formed precipitate was isolated through centrifugation and rinsed with methanol and n-hexane for three times, and then dried under vacuum at 25 °C overnight to obtain a brown solid (62 mg, 68 %).

SCPNs from $SCPN_{(12)}$ to $SCPN_{(73)}$ were prepared following a similar procedure as that for $SCPN_{(63)}$. When $A_{(1)}$, $A_{(6)}$ or $A_{(7)}$ was included, the reaction temperature was set as 110 °C.

Preparation of $SCPN_{(44)}$



2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (94.8 mg, 0.15 mmol), Pd@SS-CNMs (10 mg, 1.5×10^{-3} mmol of Pd), 3,4-bis(octyloxy)thiophene (102 mg, 0.3 mmol) and tetrabutylammonium fluoride hydrate (663 mg, 2.1 mmol) were successively added to a 10 ml sealed tube and dried at room temperature for 30 min. Pivalic acid (10 μl) and DMAc (2 ml) were carefully dropped into the tube under nitrogen atmosphere. After three freeze-pump-thaw circles, the tube was sealed. The mixture was stirred at 100 °C for 120 h. After removal of the heterogeneous catalysts by centrifugation, the supernatant was concentrated and added dropwise into methanol (60 ml). The precipitate was isolated through centrifugation and washed with methanol and n-hexane for three times. Yellow solid was obtained after drying *in vacuo* overnight (72 mg, 57 %). Other $SCPN_{(x4)}$ were prepared following a similar procedure as that for $SCPN_{(44)}$. When $A_{(1)}$, $A_{(6)}$ or $A_{(7)}$ was included, the reaction temperature was set as 110 °C.

General procedure to build up the complete SCPN library through postmodification.

1) **Postmodification with EDOT ($SCPN_{(63)}E$):** S$CPN_{(63)}$ (40 mg), $Pd(OAc)_2$ (3 mg, 0.013 mmol), KOAc (46 mg, 0.47 mmol), tetrabutylammonium bromide (TBAB, 60 mg, 0.14 mmol) were added to a 10 ml sealed tube. DMAc (8 ml) was carefully dropped into the tube under nitrogen atmosphere. After two freeze-pump-thaw circles, the mixture was frozen by liquid nitrogen and EDOT (200 μL, 1.6 mmol) was injected under nitrogen atmosphere. Then several vacuum pumping and nitrogen filling cycles were conducted. Finally the tube was sealed in nitrogen atmosphere. After stirred at 90 °C for 5 h, the resulting orange mixture was diluted with dichloromethane (DCM,

40 mL), then washed with saturated NaCl aqueous solution (3×40 mL) and dried over anhydrous $MgSO_4$. The filtrate was concentrated and reprecipitated with methanol. The formed precipitate was isolated through centrifugation and rinsed with methanol for three times and then dried *in vacuo* overnight to obtain brown solid (30 mg).

2)**Terminal modification with $T_{(5)}$ ($SCPN_{(63)}E_{(5)}$):** $SCPN_{(63)}E$ (15 mg), 2,2,2-trifluoro-1-(4-iodo-phenyl)-ethanone ($T_{(5)}$, 80 mg, 0.32 mmol), $Pd(OAc)_2$ (3 mg, 0.013 mmol), KOAc (13 mg, 0.13 mmol), TBAB (18 mg, 0.056 mmol) were added to a 10 ml sealed tube. DMAc (2 ml) was carefully dropped into the tube under nitrogen atmosphere. After three freeze-pump-thaw circles, the tube was sealed under N_2 atmosphere and stirred at 90 °C for 5 h. The resulting red mixture was diluted with DCM (40 mL), washed with saturated NaCl aqueous solution (3×40 mL), and dried over anhydrous $MgSO_4$. The filtrate was concentrated and reprecipitated with methanol. The formed precipitate was isolated through centrifugation and rinsed with methanol for three times and then dried under vacuum at 25 °C overnight to obtain orange red solid (14 mg).

Some of the members in the primary SCPN library could be used directly for terminal modification without reacting with EDOT. In those cases, the $SCPN_{(xy)}$ obtained from the confined polycondensation reacted with $T_{(z)}$ directly following the above mentioned procedures to give the $SCPN_{(xyz)}$ products .

Postmodification of $SCPN_{(63)}$ with anthracen-9-ylboronic acid($T_{(1)}$)

$SCPN_{(63)}$ (20 mg), anthracen-9-ylboronic acid (88.8 mg, 0.4 mmol), K_3PO_4 (127 mg, 0.6 mmol), $Pd(PPh_3)_4$ (10 mg, 0.01 mmol) were successively added to a 10 ml sealed tube and DMAc (2 ml) were carefully dropped into the tube under nitrogen atmosphere. After three freeze-pump-thaw circles, the tube was sealed. The mixture was stirred at 100 °C for 4.5 h. The resulting mixture was diluted with DCM (40 mL), washed with saturated NaCl aqueous solution (3×40 mL), and dried over anhydrous $MgSO_4$. The filtrate was concentrated and reprecipitated with methanol. The formed precipitate was isolated through centrifugation and rinsed with methanol for three times and then dried under vacuum at 25 °C overnight to obtain orange solid (11.5 mg).

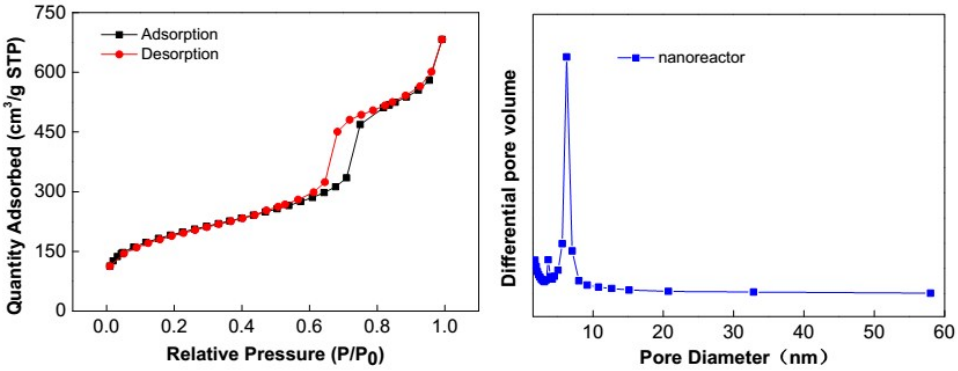


Fig. S1 Nitrogen adsorption–desorption isotherm of the nanoreactors (Pd@SS-CNMs) at 77 K and pore size distribution calculated by the BJH desorption approach.

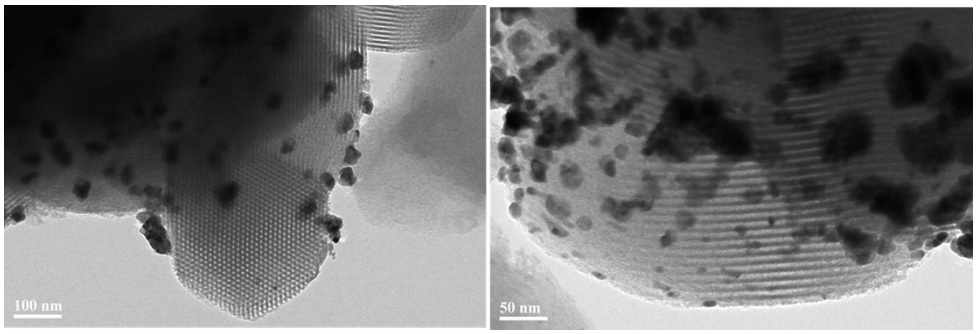


Fig. S2 HR-TEM images of the Pd nanoparticles with SS-CNMs support of a control group (Pd/SS-CNM), where a similar preparation method was used to that of Pd@SS-CNMs nanoreactors, except that the Pd precursor (H_2PdCl_4) outside of the channels of the SS-CNMs was not washed away. The Pd species outside of the channels clearly tends to aggregate and exhibit irregular shapes.

Table S1 Combinatorial polymerization to build up the primary library.

$SCPN_{(xy)}$	$A_{(x)}+B_{(y)}$	Yield	M_n (PDI)[a]	FQY	K_{sv}^{PA}	Band gapd
11	1+1	52%	1560 (1.4)	0.08[b]	82817	3.14 eV
21	2+1	24%	1639 (1.4)	0.19[b]	25685	3.47 eV
31	3+1	87 %	1413 (1.3)	0.21[b]	18270	3.06 eV
41	4+1	55%	1653 (1.1)	0.34[b]	31825	3.25 eV
51	5+1	35%	1177 (1.2)	0.32[b]	30510	3.08 eV
61	6+1	47%	1948 (1.5)	0.24[b]	18148	3.05 eV
71	7+1	21%	1509 (1.5)	0.37[b]	17403	3.05 eV
12	1+2	19%	1515 (1.1)	0.05[b]	94118	3.96 eV
22	2+2	64 %	2022 (1.3)	0.46[b]	74137	3.73 eV
32	3+2	45 %	1606 (1.1)	0.39[b]	110175	3.47 eV
42	4+2	5 %	1688 (1.1)	0.18[b]	31755	3.12 eV
52	5+2	51 %	1963 (1.3)	0.27[b]	38131	3.32 eV
62	6+2	18%	1845 (1.1)	0.13[b]	25190	3.07 eV
72	7+2	40 %	1613 (1.8)	0.09[b]	30235	2.81 eV
13	1+3	51 %	1568 (1.3)	0.10[b]	87355	3.06 eV
23	2+3	68 %	2327 (1.4)	0.27[b]	50114	2.91 eV
33	3+3	69%	1707 (1.8)	0.12[b]	26162	3.06 eV
43	4+3	83%	1800 (1.5)	0.85[b]	16352	2.64 eV
53	5+3	60%	1909 (1.5)	0.78[b]	8846	2.64 eV
63	6+3	68 %	1890 (1.4)	0.04[c]	17984	2.62 eV
73	7+3	52%	1650 (1.6)	0.14[c]	28643	2.39 eV
14	1+4	30%	2702 (1.3)	0.07[b]	11523	3.14 eV
24	2+4	68%	2600 (1.2)	0.31[b]	52257	2.99 eV
34	3+4	52%	2711 (1.2)	0.28[b]	48357	3.19 eV
44	4+4	57%	2508 (1.3)	1.05[b]	22675	2.76 eV
54	5+4	71%	2586 (1.4)	0.63[b]	10979	2.72 eV
64	6+4	52 %	2134 (1.1)	0.08[c]	30158	2.63 eV
74	7+4	45%	2271 (1.1)	0.09[c]	19155	2.63 eV

[a)] Measured by GPC; [b)] using quinine sulfate as the standard (excited at 350 nm); [c)] using fluorescein as the standard (excited at 440 nm); [d)] from Kubelka–Munk function versus the energy of exciting light.

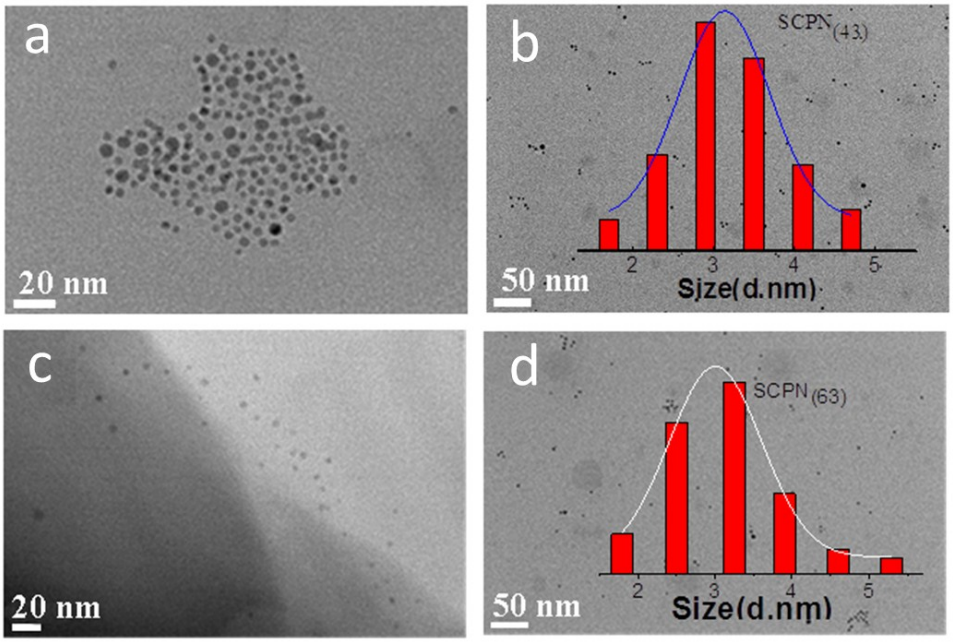


Fig. S3 (a, b) HR-TEM and size histogram of $SCPN_{(43)}$, 3.3 nm. (c, d) $SCPN_{(63)}$, 3.2 nm..

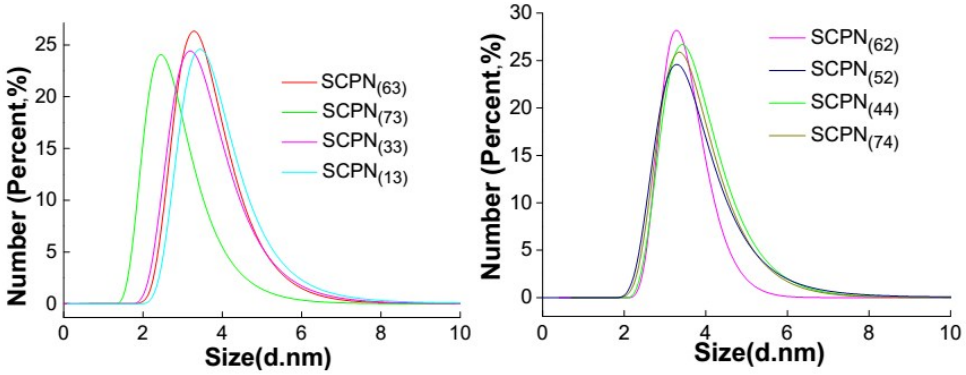


Fig. S4 Size distributions of SCPNs measured by dynamic light scattering in THF solution. All SCNPs have a size of about 3.0 nm, except for $SCNP_{(73)}$ (2.1 nm), which contains planar pyrene units.

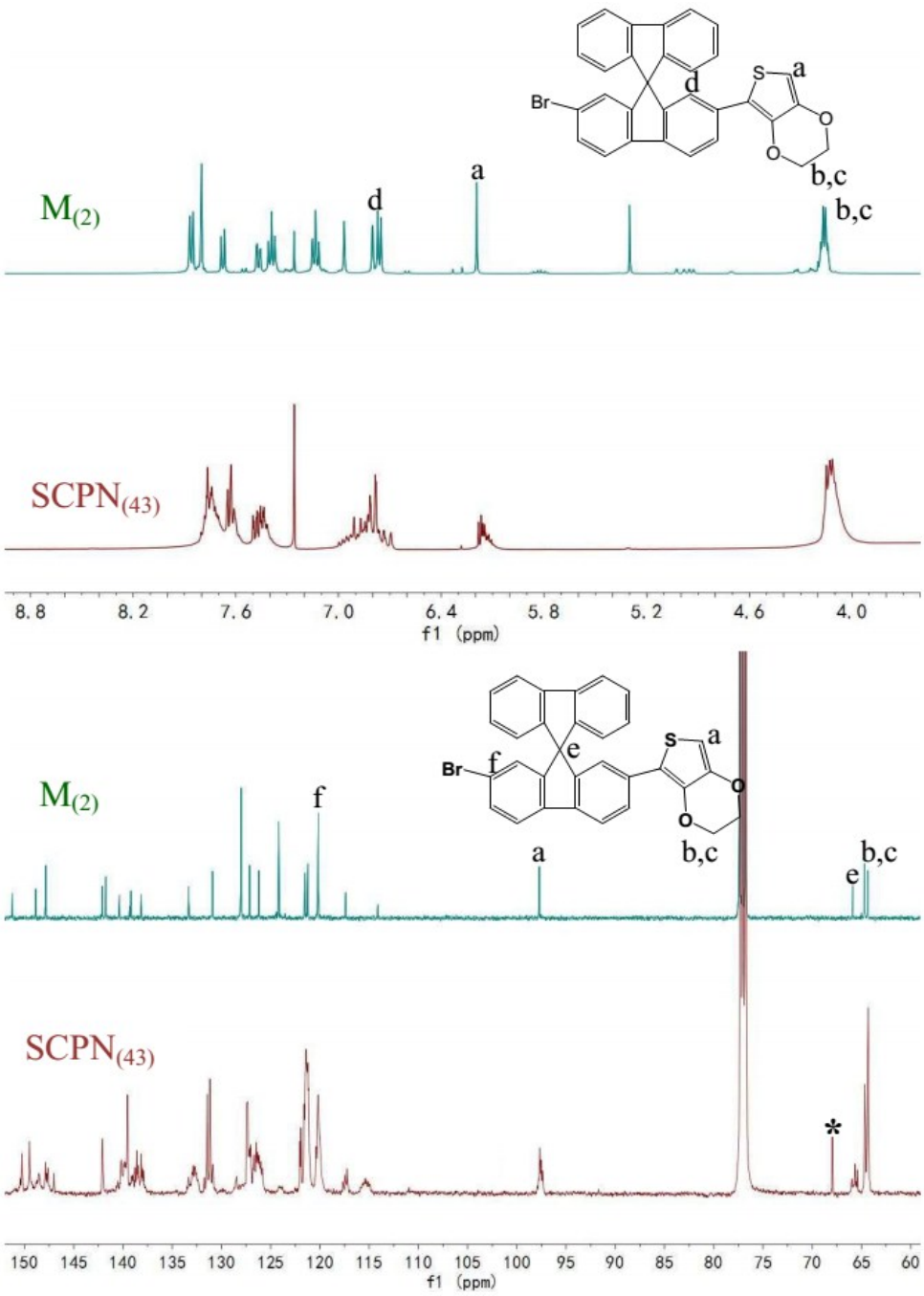


Fig. S5 Comparison of ^{1}H NMR and ^{13}C NMR spectra of $M_{(2)}$ and $SCPN_{(43)}$ in $CDCl_3$. The asterisks (*) indicate the solvent residue (tetrahydrofuran).

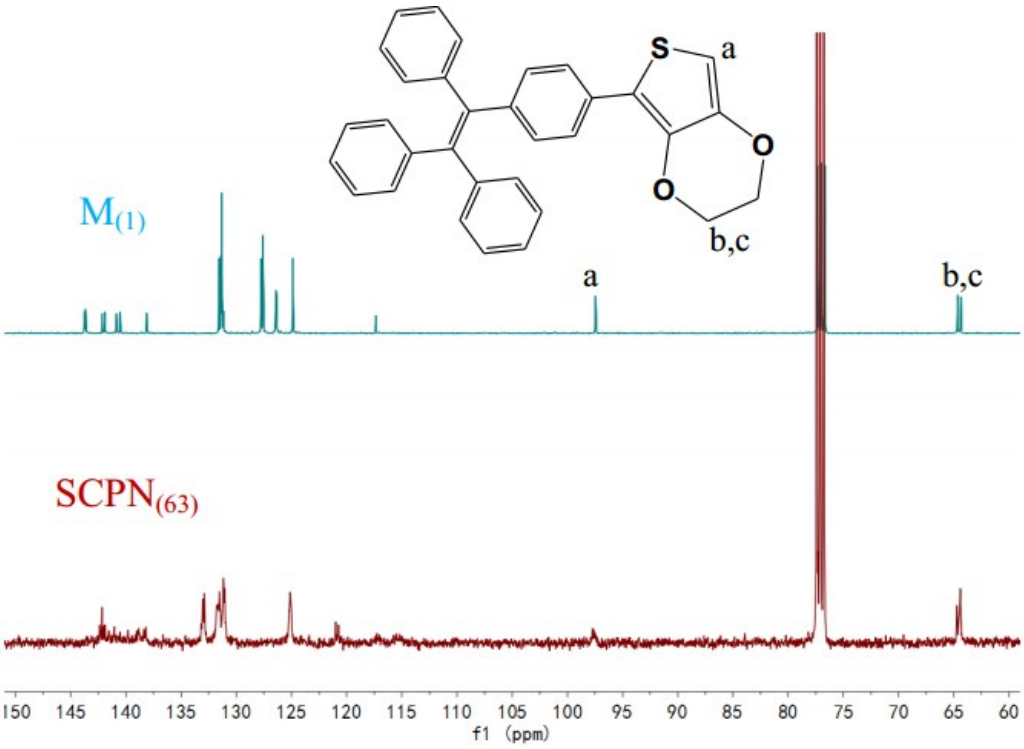


Fig. S6 Comparison of ^{13}C NMR spectra of $M_{(1)}$ and $SCPN_{(63)}$ in $CDCl_3$.

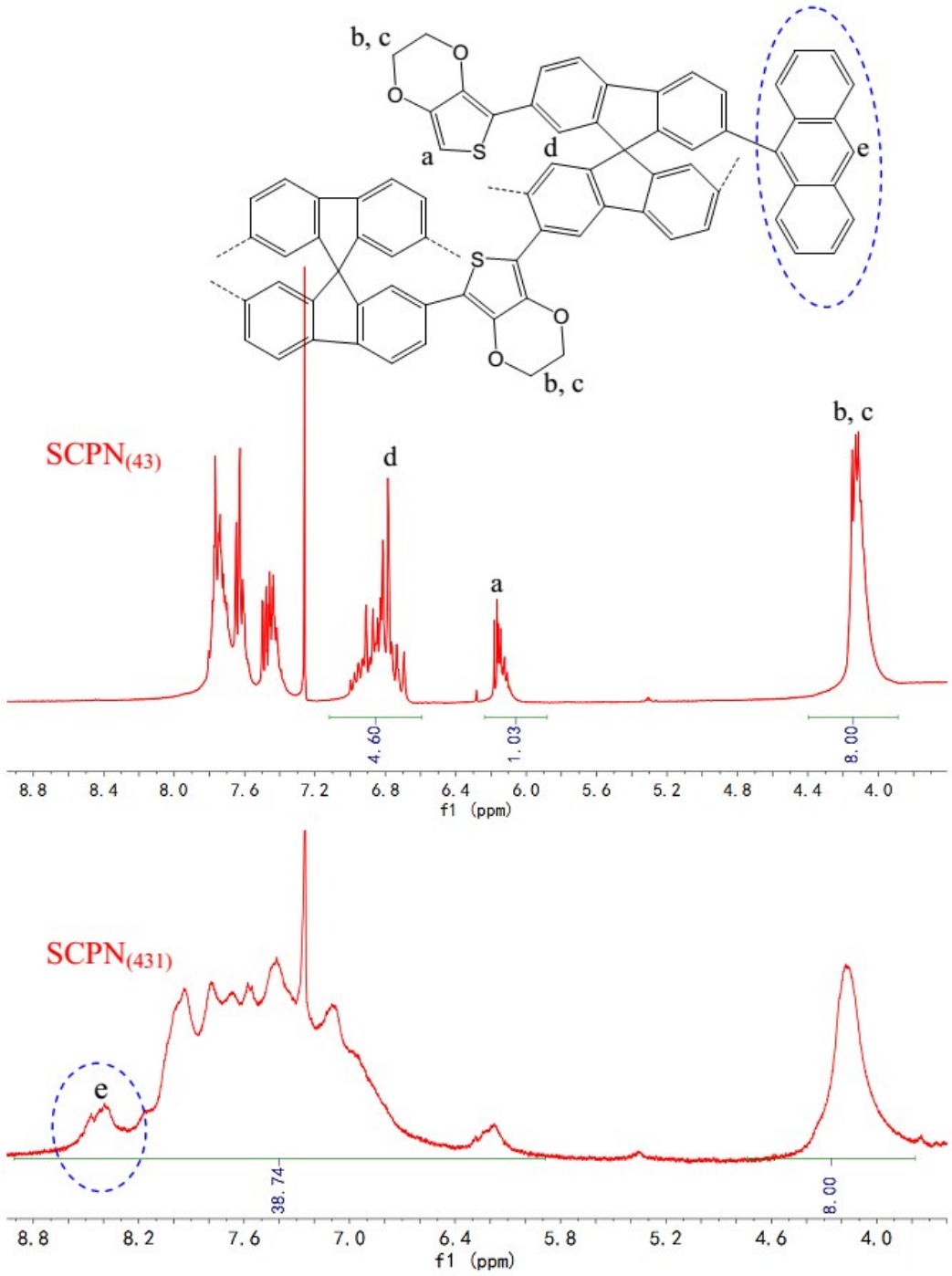


Fig. S7 The ^{1}H NMR integral calculation of the composition of $SCPN_{(43)}$, 9,9'-spirobifluorene units : EDOT units : aromatic bromine : end thiophene hydrogen (a) = 1.1 : 2.0 : 2.5 : 1.0.

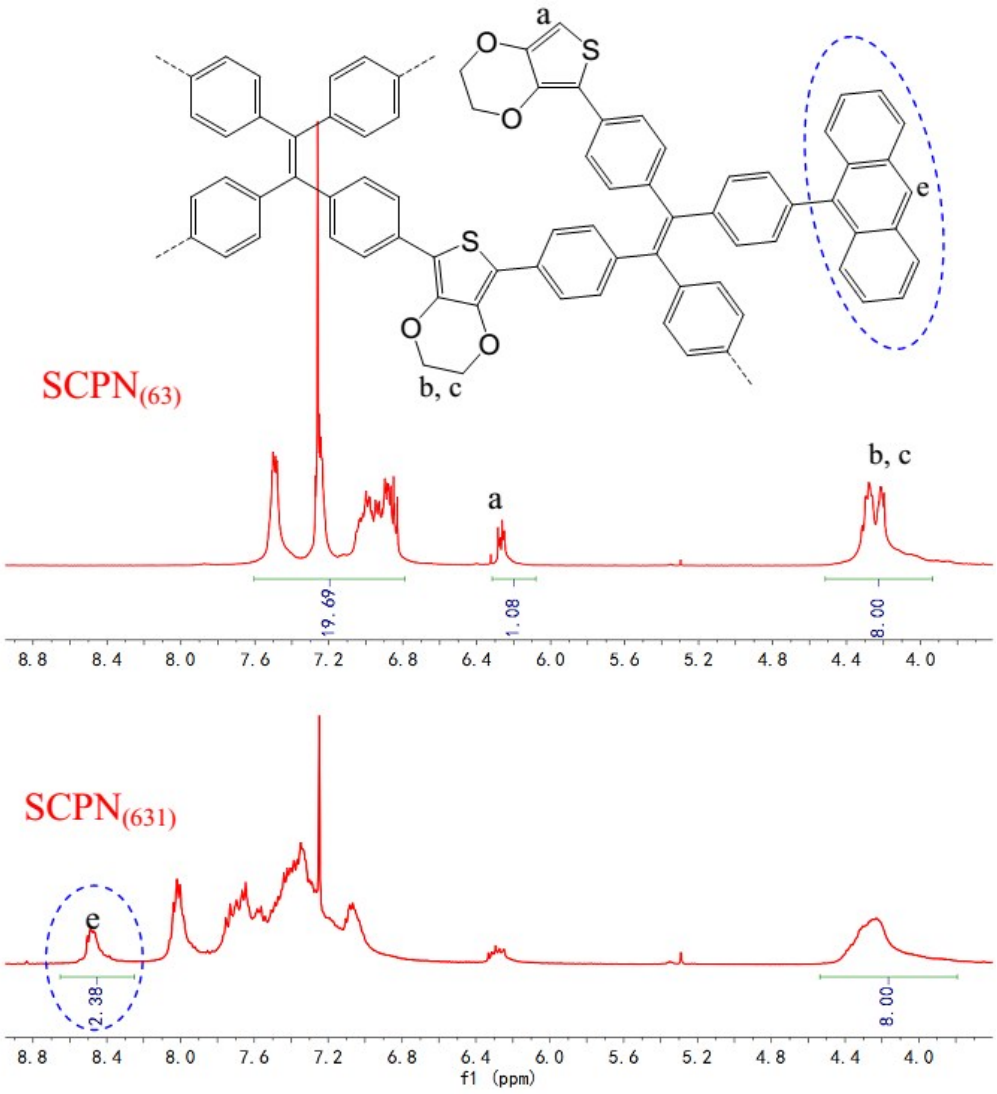


Fig. S8 The ^{1}H NMR integral calculation of the composition of $SCPN_{(63)}$, 1,1,2,2-tetraphenylethene units : EDOT units : aromatic bromine : end hydrogen of thiophene=1.2 : 2.0 : 2.4 : 1.1.

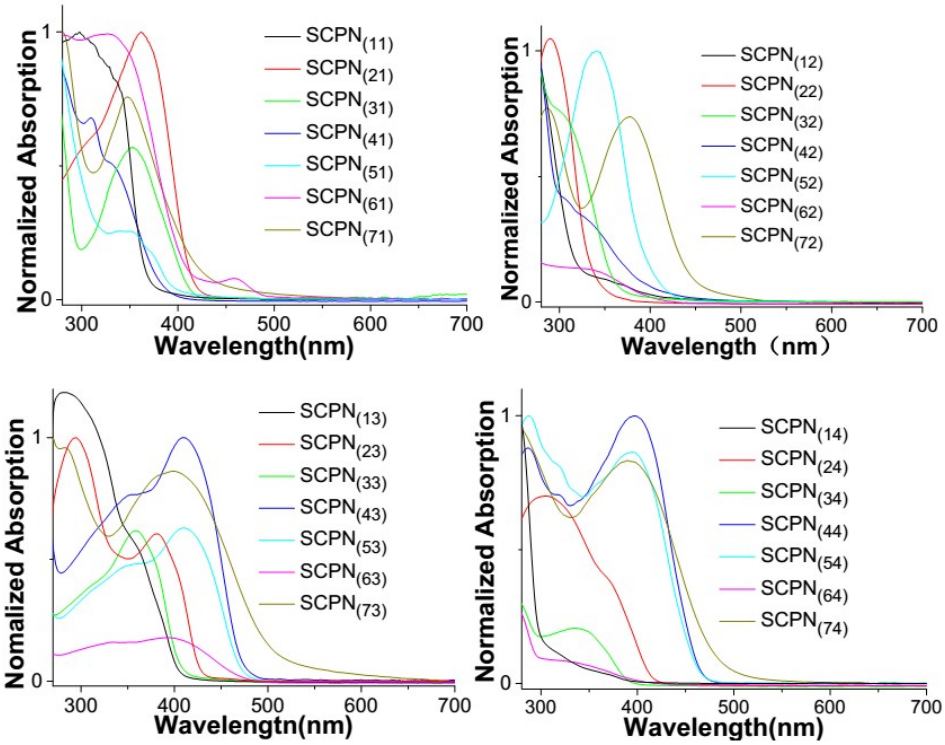


Fig. S9 UV-Vis absorption spectra of SCPNs of the primary library in DMF at room temperature.

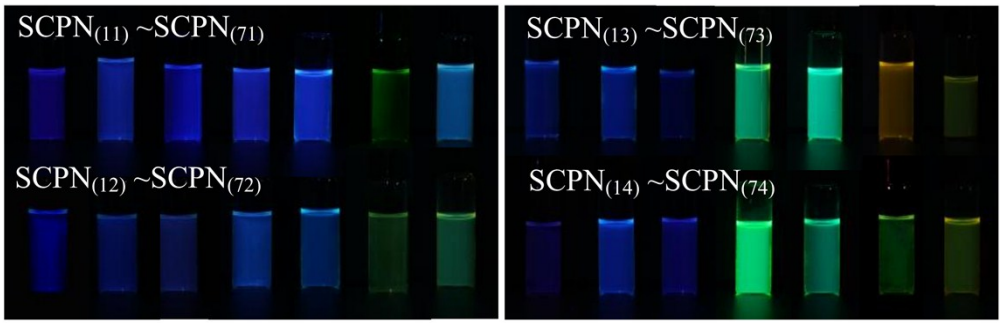


Fig. S10 Solutions of SCPNs in THF show bright luminescence from blue to yellow under UV irradiation (365 nm).

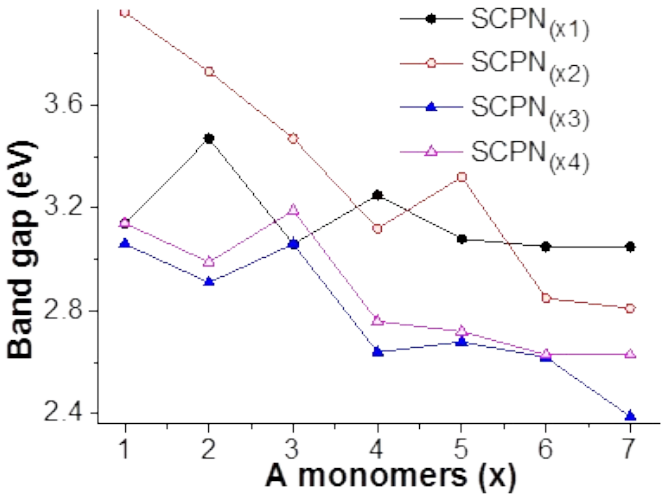


Fig. S11 Tunable band gap by varying monomers, x changes from $A_{(1)}$ to $A_{(7)}$.

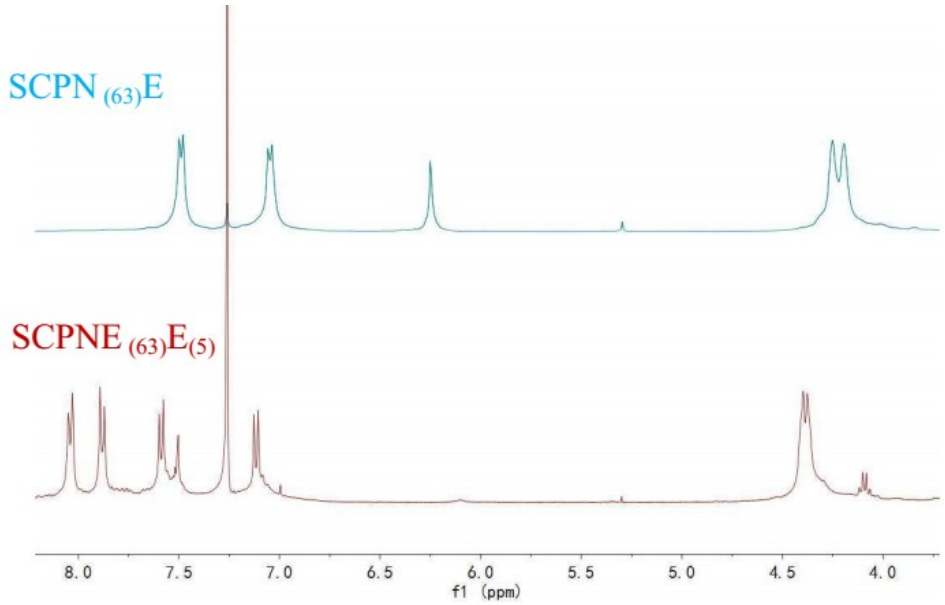


Fig. S12 The ^{1}H NMR spectra of $SCPN_{(63)}E$ and $SCPN_{(63)}E_{(5)}$ in $CDCl_3$.

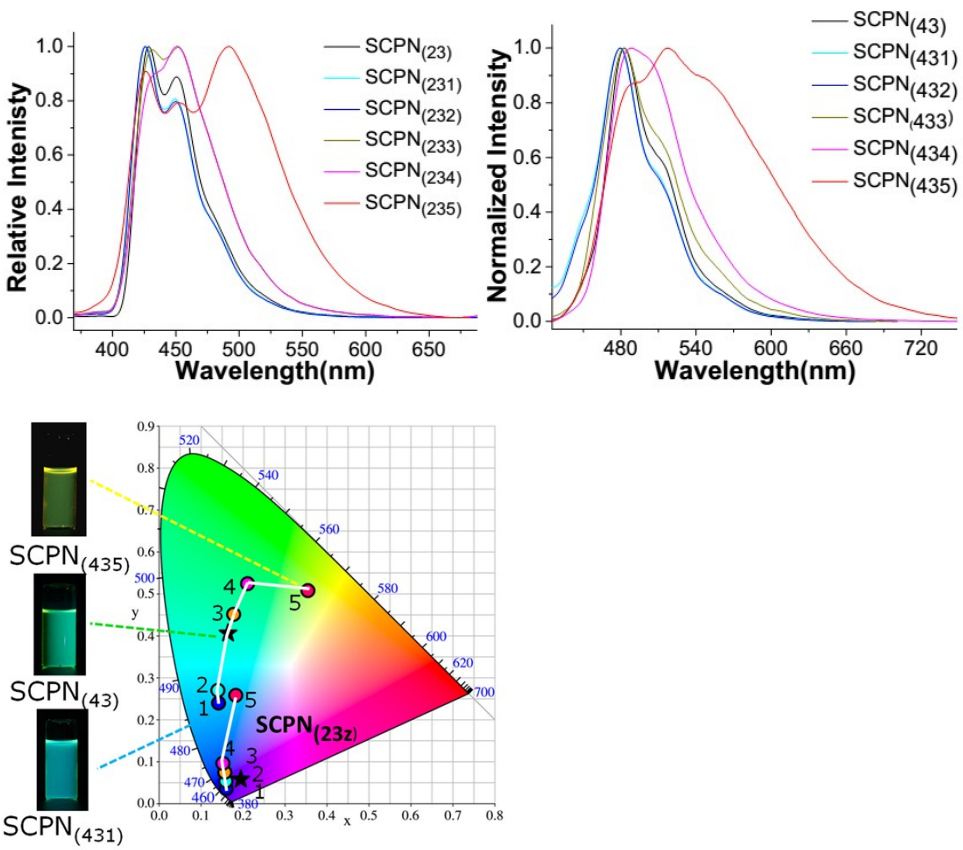


Fig. S13 Tunable fluorescence emission of $SCNP_{(23)}$ and $SCNP_{(43)}$ by the introduction of varied terminals (T(z) , z=1~5).

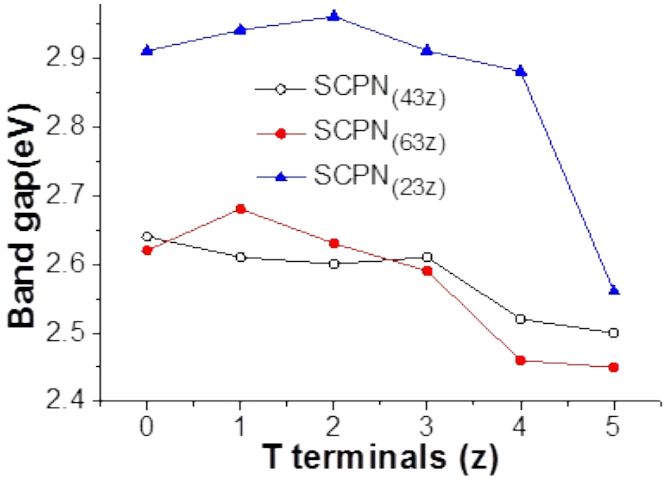


Fig. S14 Tunable band gap by varying terminals (z).

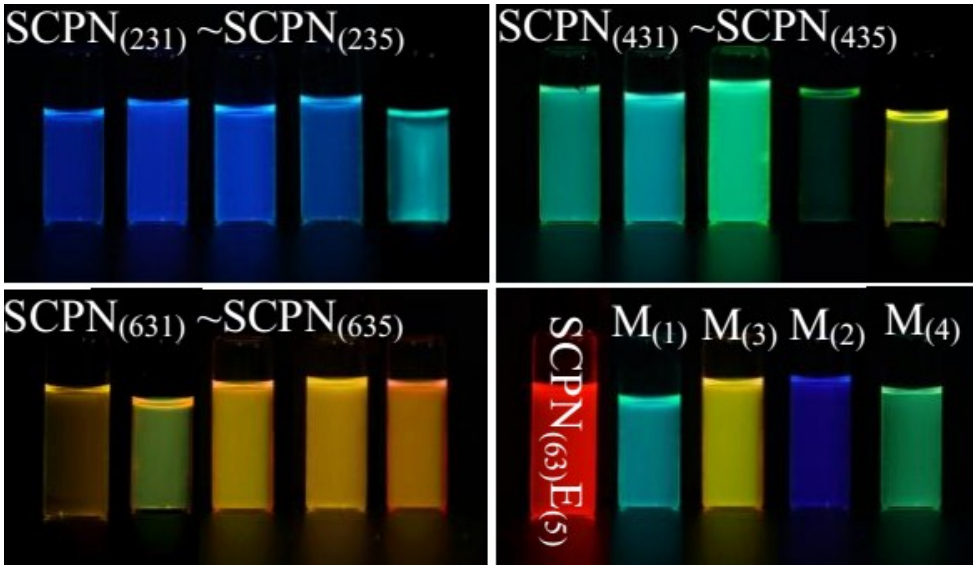


Fig. S15 Fluorescence images of $SCPN_{(23z)}$, $SCPN_{(43z)}$, $SCPN_{(63z)}$ ($0<z\leq5$), $SCPN_{(23)}E$ and model compounds in THF show bright luminescence from blue to red under UV irradiation (365 nm).

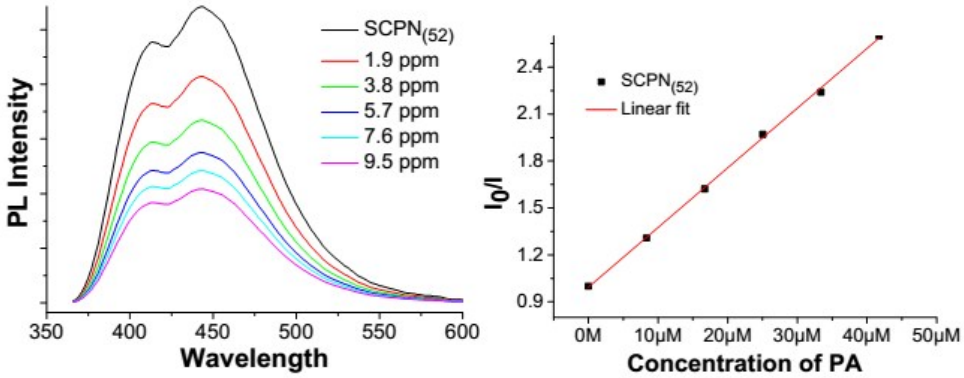
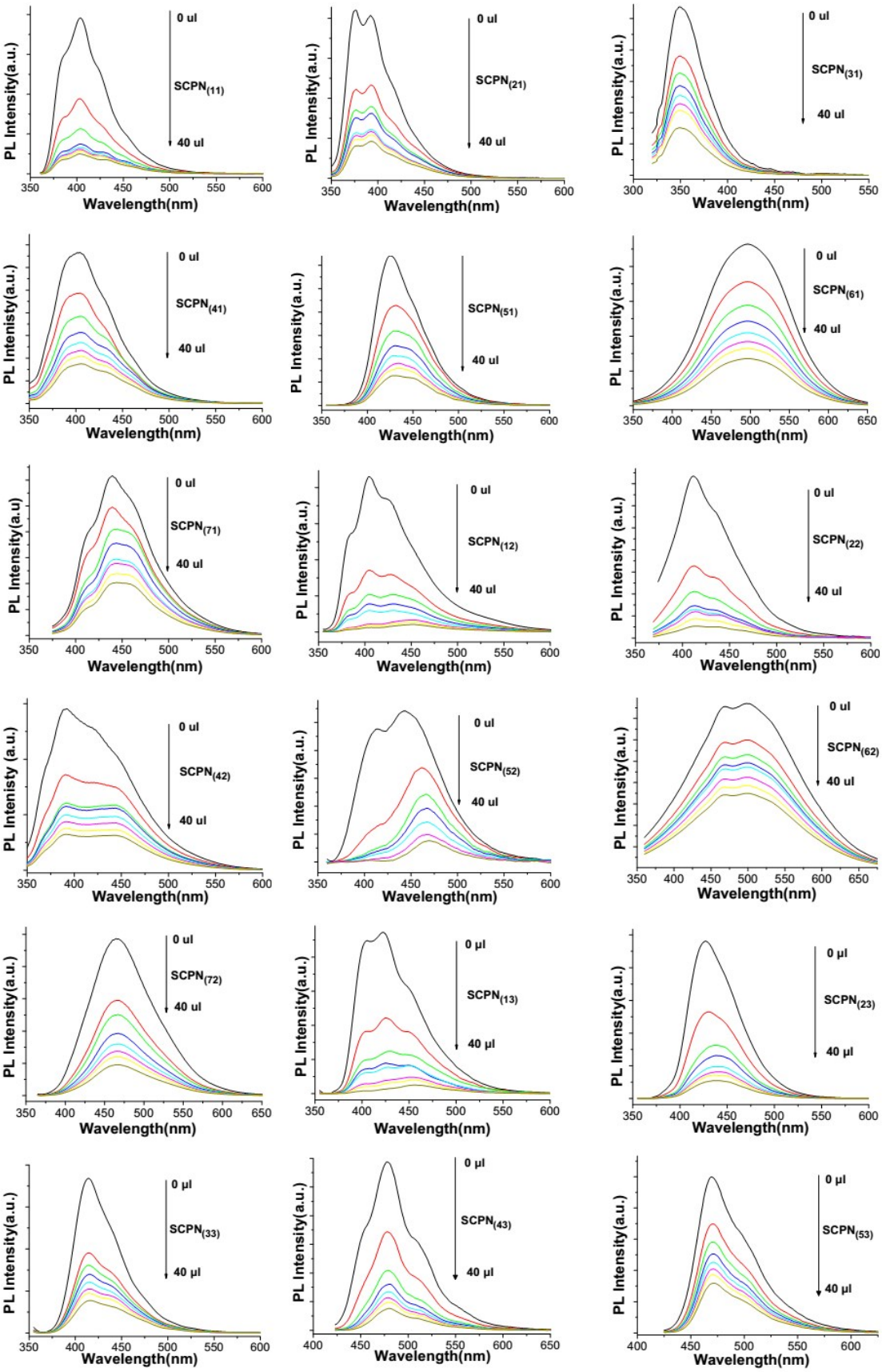
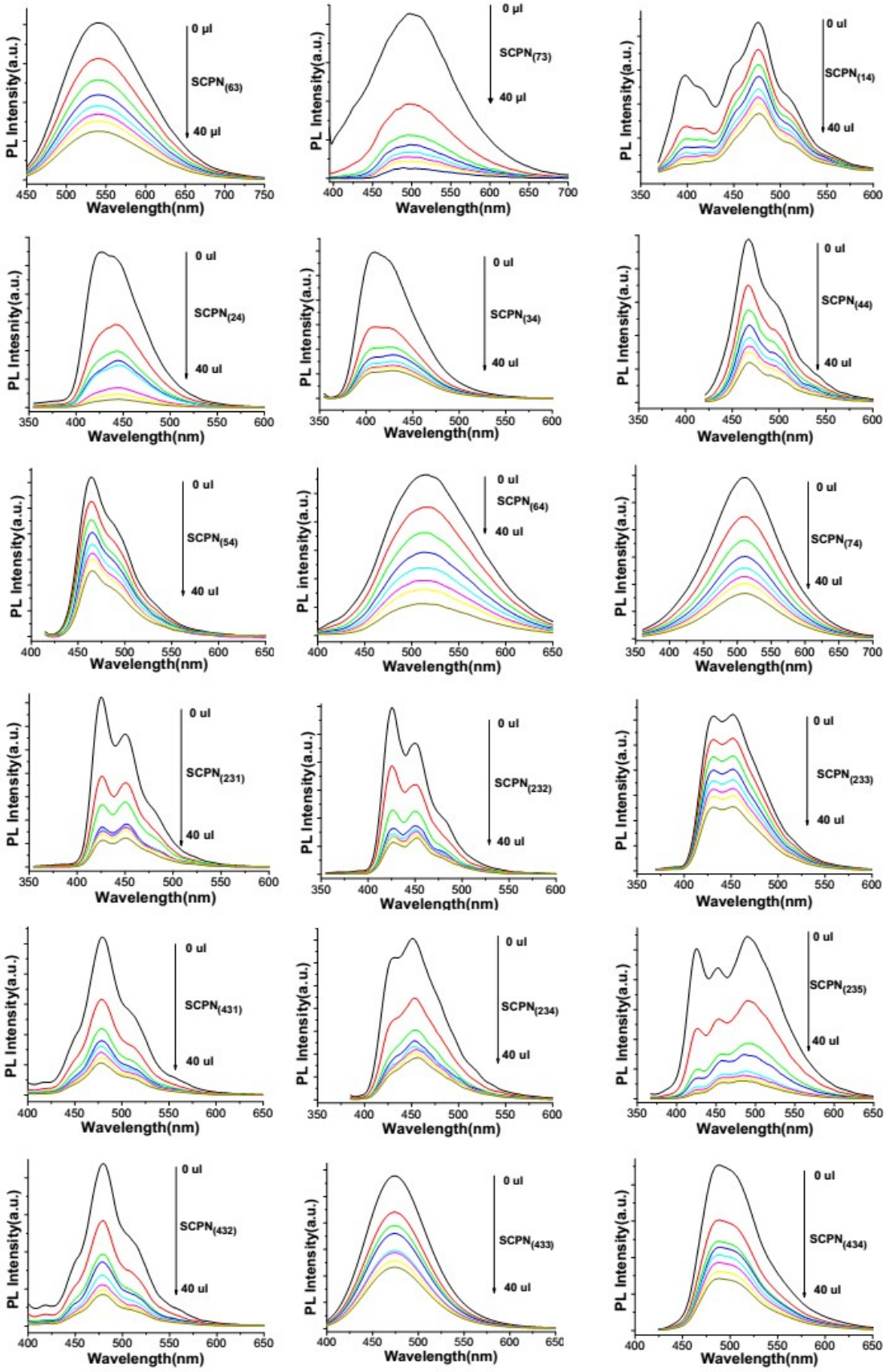


Fig. S16 Fluorescence quenching titration experiments of $SCPN_{(52)}$ with PA(left) and Stern Volmer plot (right).


PL Intensity(a.u.)
Wavelength(nm)
0 ul
SCPN(11)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
0 ul
SCPN(21)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
0 ul
SCPN(31)
40 ul
PL Intenisty(a.u.)
Wavelength(nm)
0 ul
SCPN(41)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
SCPN(51)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
0 ul
SCPN(61)
40 ul
PL Intensity(a.u)
Wavelength(nm)
0 ul
SCPN(71)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
0 ul
SCPN(12)
40 ul
PL Intensity (a.u.)
Wavelength(nm)
0 ul
SCPN(22)
40 ul
PL Intensty (a.u.)
Wavelength(nm)
0 ul
SCPN(42)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
0 ul
SCPN(52)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
0 ul
SCPN(62)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
0 ul
SCPN(72)
40 ul
PL Intensity(a.u.)
Wavelength(nm)
0 µl
SCPN(13)
40 µl
PL Intensity(a.u.)
Wavelength(nm)
0 µl
SCPN(23)
40 µl
PL Intensity(a.u.)
Wavelength(nm)
0 µl
SCPN(33)
40 µl
PL Intensity(a.u.)
Wavelength(nm)
0 µl
SCPN(43)
40 µl
PL Intensity(a.u.)
Wavelength(nm)
0 µl
SCPN(53)
40 µl


PL Intensity(a.u.)
Wavelength(nm)
0 µl
SCPN(63)
40 µl
0 µl
SCPN(73)
40 µl
0 ul
SCPN(14)
40 ul
0 ul
SCPN(24)
40 ul
0 ul
SCPN(34)
40 ul
0 ul
SCPN(44)
40 ul
0 ul
SCPN(54)
40 ul
0 ul
SCPN(64)
40 ul
0 ul
SCPN(74)
40 ul
0 ul
SCPN(231)
40 ul
0 ul
SCPN(232)
40 ul
0 ul
SCPN(233)
40 ul
0 ul
SCPN(431)
40 ul
0 ul
SCPN(234)
40 ul
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0 ul
SCPN(433)
40 ul
0 ul
SCPN(434)
40 ul

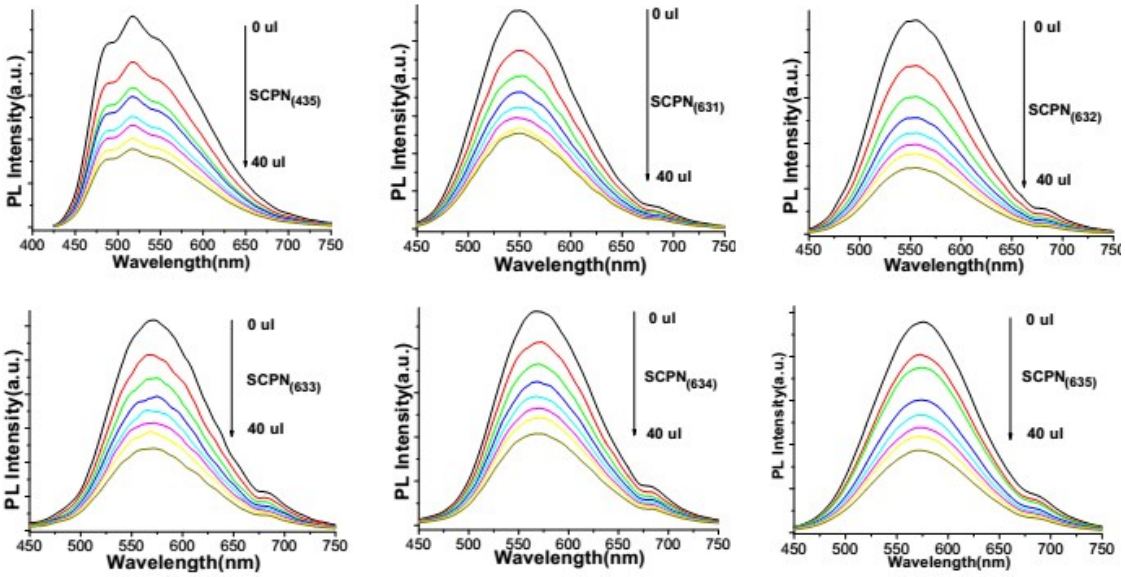

Fig. S17 Fluorescence quenching titration experiments with PA, the fluorescence of all the SCPNs were quenched obviously with the addition of THF solution of PA (10 mM).

Table S2 HOMO and LUMO level data of SCPNs.

SCPNs	HOMO	LUMO	Band gap	ΔG_0
$SCPN_{(51)}$	-5.19 eV[a]	-2.11 eV	3.08 eV[b]	-2.20 eV
$SCPN_{(32)}$	-5.24 eV[a]	-1.77 eV	3.47 eV[b]	-2.54 eV
$SCPN_{(52)}$	-5.25 eV[a]	-1.93 eV	3.32 eV[b]	-2.38 eV
$SCPN_{(63)}$	-5.35 eV[a]	-2.73 eV	2.62 eV[b]	-1.58 eV
$SCPN_{(23)}$	-5.35 eV[a]	-2.44 eV	2.91 eV[b]	-1.87 eV
$SCPN_{(24)}$	-5.32 eV[a]	-2.33 eV	2.99 eV[b]	-1.98 eV
PA	-8.62 eV[c]	-4.31 eV	2.54 eV[c]	

a) Measured by cyclic voltammetry; b) From Kubelka–Munk function versus the energy of exciting light; c) Calculated using B3LYP/6-31G* as the basis sets (Gaussian09).

Table S3 Fluorescence lifetime (ns) titration of $SCPN_{(32)}$ with the addition of PA.

PA	τ_1	β_1	τ_2	β_2	Average
0	0.83	0.30	5.70	0.70	4.24 ns
4.8 ppm	0.82	0.28	5.62	0.71	4.21 ns
9.5 ppm	0.63	0.26	4.91	0.74	3.80 ns

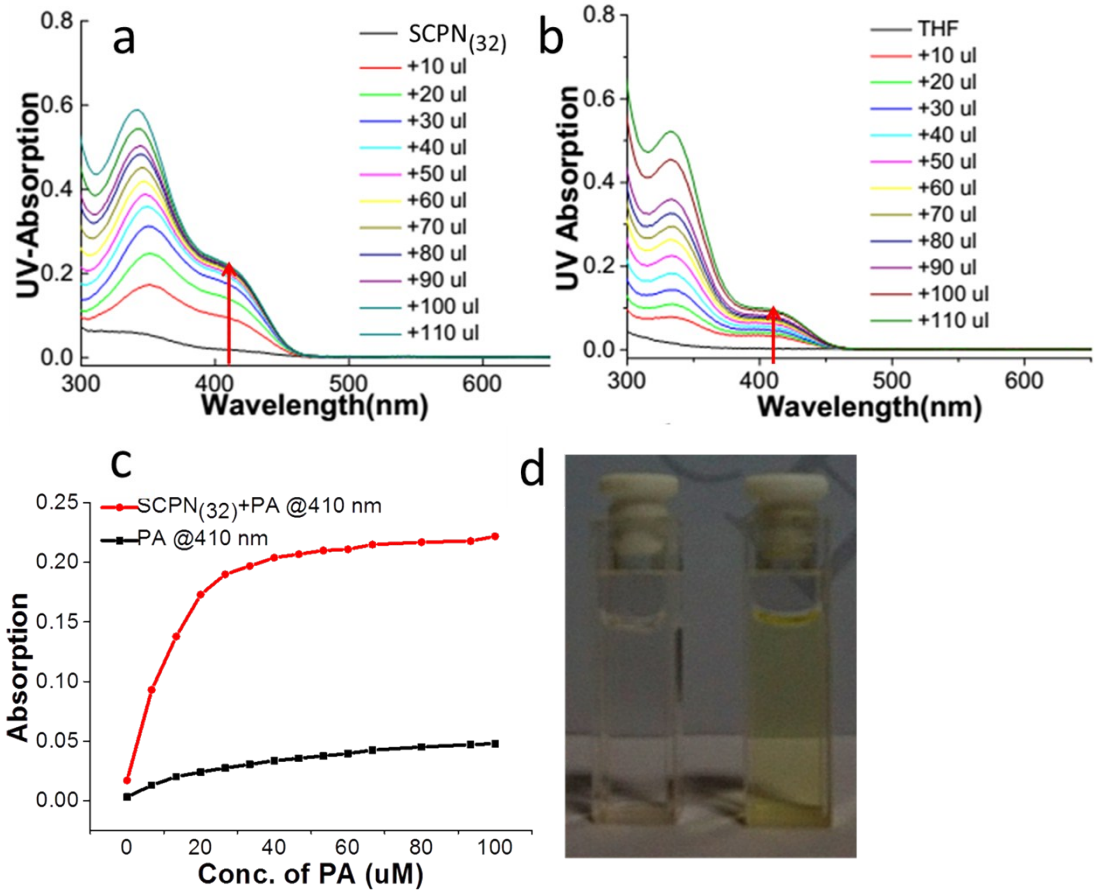

Fig. S18 (a) Ultraviolet absorption titration of $SCPN_{(32)}$ with the addition of picric acid (PA, 10 mM). (b) A blank sample titration experiments, none was added except PA. (c) The enhanced absorption of $SCPN_{(32)}$ at 410 nm in comparison with blank sample when triated with PA. (d) Color change from colorless to yellow when $SCPN_{(32)}$ was titrated with PA, the left cuvette was a result of blank sample where only solution of PA was added and the right cuvette contained $SCPN_{(32)}$ and picric acid.

Table S4. K_{sv} and band gap values of SCPNs after postmodification.

$SCPN_{(xyz)}$	K_{sv}	Band gap[a]
23	50114	2.91 eV
231	51609	2.94 eV
232	48342	2.96 eV
233	32000	2.91 eV
234	32232	2.88 eV
235	31000	2.56 eV
43	16352	2.64 eV
431	34138	2.61 eV
432	24788	2.60 eV
433	12216	2.61 eV
434	12992	2.52 eV
435	12311	2.5 eV
63	15768	2.62 eV
631	16500	2.68 eV
632	16691	2.63 eV
633	11798	2.59 eV
634	10092	2.46 eV
635	11872	2.45 eV

[a)]From Kubelka–Munk function versus the energy of exciting light.

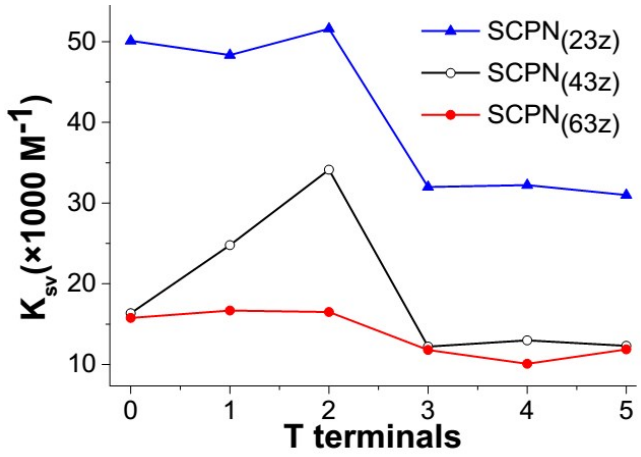

Fig. S19 K_{sv} value changes according to the variation of $T_{(z)}$ terminals.

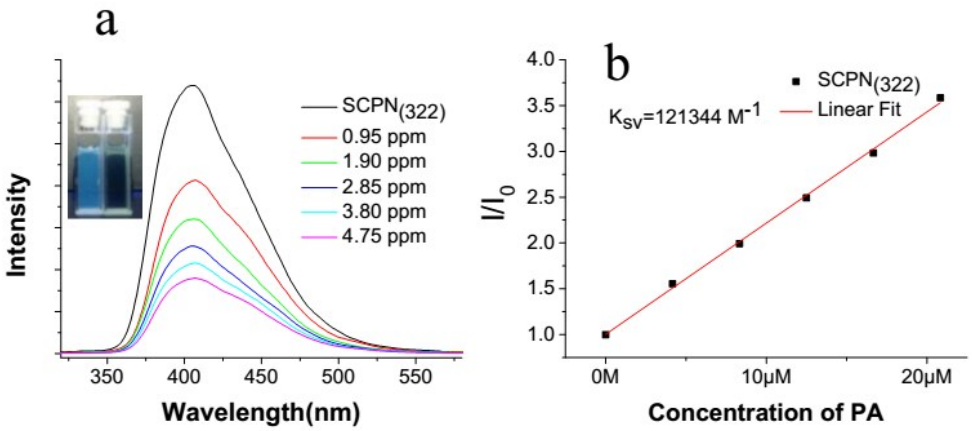

Fig. S20 (a) Fluorescence quenching titration experiments with PA, the fluorescence of $SCPN_{(322)}$ were quenched obviously with the addition of a THF solution of PA (2.5 mM). (b) Stern Volmer curve of $SCPN_{(322)}$ when titrated with PA.

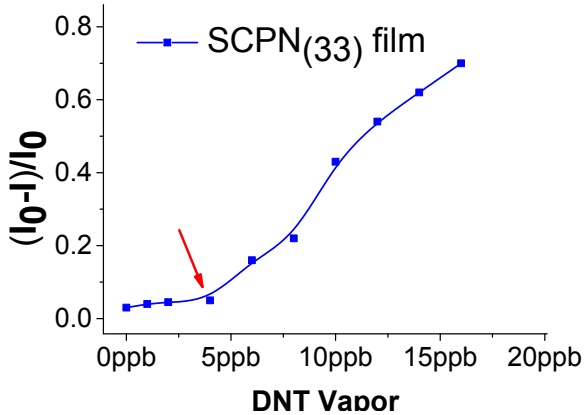

Figure. S21 Fluorescence intensity of $SCPN_{(33)}$ at 500 nm as a function of vapor concentration (DNT).

Calculation of HOMO and LUMO energy level of PA.

Calculations for HOMO and LUMO energy levels of PA were carried out using B3LYP/6-31G* as the basis sets (Gaussian 09).

Reference:

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