

Supporting information

Porosity induced emission: exploring color-controllable fluorescence of porous organic polymers and their chemical sensing applications

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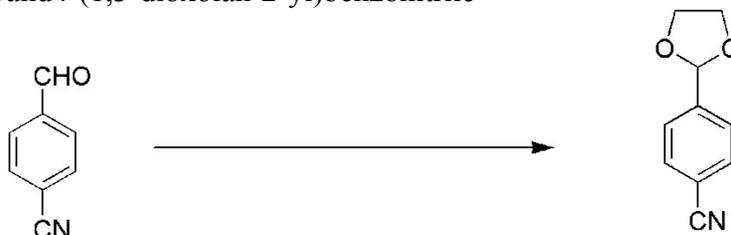
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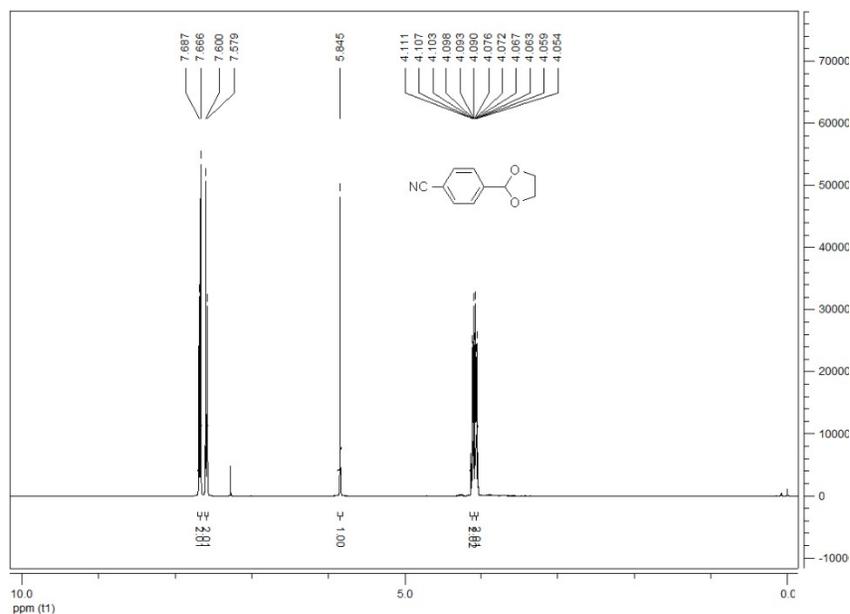
1. Experimental Section

Synthesis of monomers 4,4'-(2,5-diethyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dibenzaldehyde¹

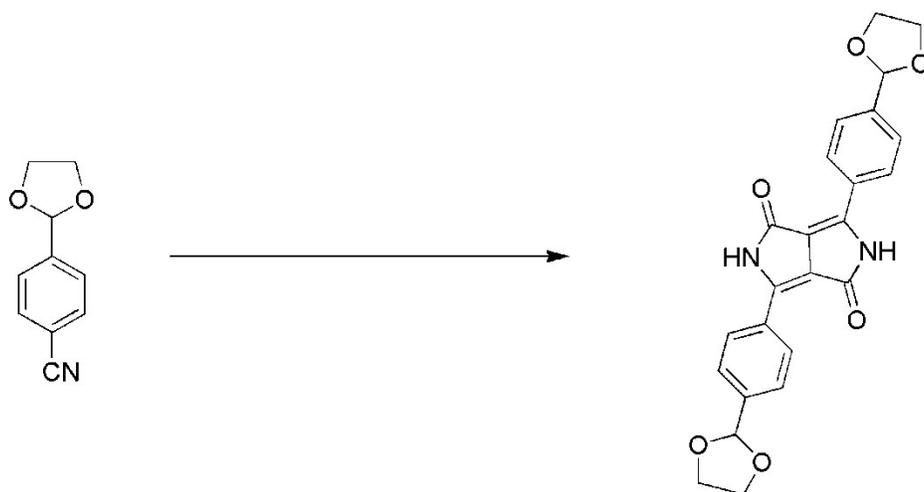
Synthesis of compound 4-(1,3-dioxolan-2-yl)benzonitrile



4-formylbenzonitrile (13.1g, 100 mmol) and glycol (18.6g, 300mmol) were dissolved in 100 mL toluene with catalytic amount of toluenesulfonic acid, then the solution was heated to 120 °C for 36 h. After the solution cool to room temperature, the solution was wash with water to remove glycol and toluenesulfonic acid. The organic phase was dried with Na₂SO₄, the solvent was evaporated in vacuum. The resulting mixture was purified by column chromatography (CH₂Cl₂/CH₃OH = 50/1) to give the title compound. ¹H NMR (400 MHz, CDCl₃): 4.06 (m, 2H), 4.10 (m, 2H), 5.08 (s, 1H), 7.59 (d, J = 8.4 Hz, 4H), 7.68 (d, J = 8.4 Hz, 4H).

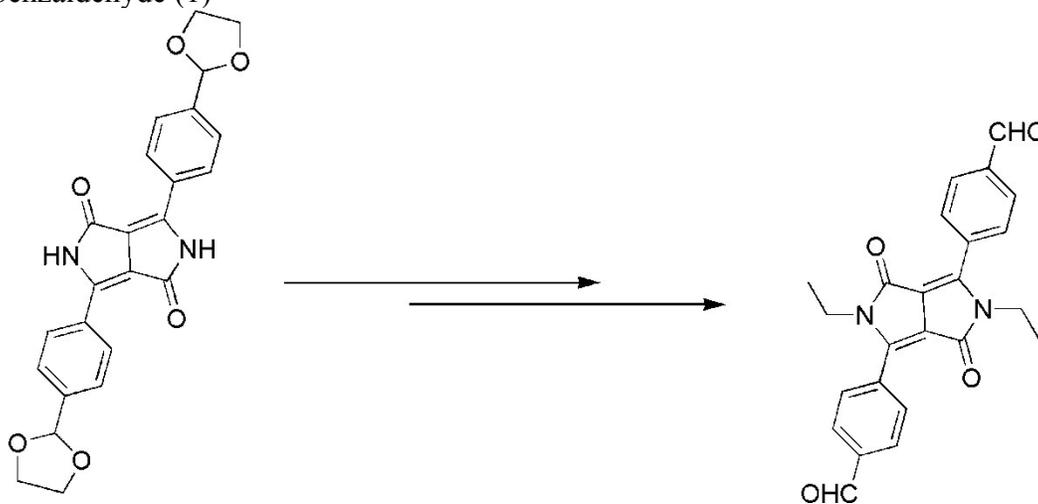


Synthesis of compound 3,6-bis(4-(1,3-dioxolan-2-yl)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione



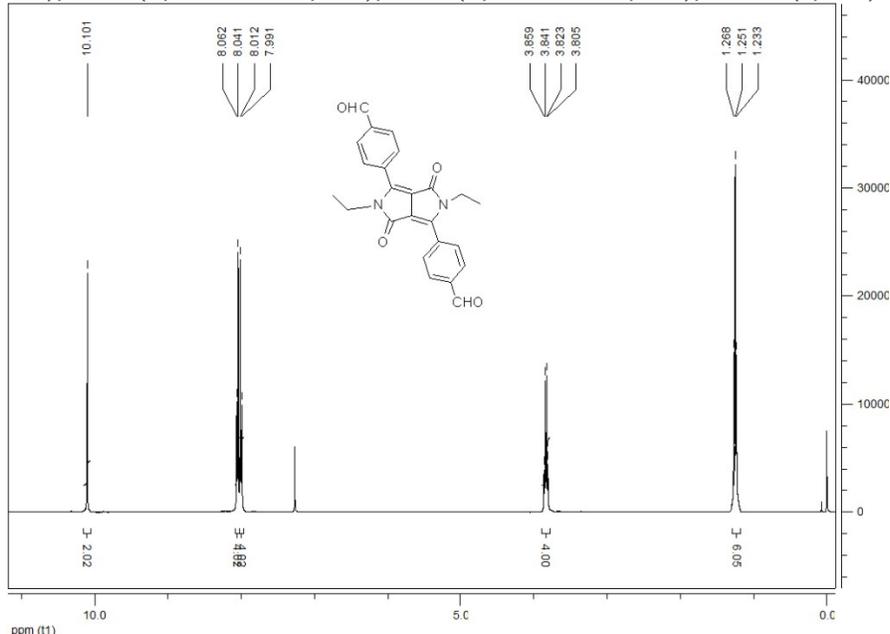
Sodium (2.30 g, 100 mmol) was dissolved in 50 mL *t*-amyl alcohol at 90 °C over 1 h with catalytic amount of FeCl₃, then the solution was cooled to 50 °C, 4-(1,3-dioxolan-2-yl)benzonitrile (7.00 g, 40 mmol) was added. The mixture was heated to 90 °C, diisopropyl succinate (4.00 g, 40 mmol) in 20 mL *t*-amyl alcohol was added dropwise over 2 h. Subsequently, the resulting suspension was kept for 3 h at 120 °C, and the mixture was cooled to room temperature. Glacial acetic acid was slowly added till pH was 7.0, after 100 mL methanol and water (1/2) added, the mixture was refluxed for 2 h. After filtration and dry, bluish-red solid was obtained (4.00 g, 30%). The product was used for next step without further purification.

Synthesis of compound 4,4'-(2,5-diethyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)dibenzaldehyde (1)



3,6-bis(4-(1,3-dioxolan-2-yl)phenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (0.22 g, 0.5 mmol), K₂CO₃ (0.27 g, 2 mmol) and 50 mL DMF were added into three-necked flask. After heated to 120 °C for 30 min, Bromoethane (1.2 g, 10 mmol) was added slowly. The mixture was stirring at 120 °C for 2 h. Then 50 mL water was poured to quench the reaction, and extracted with ethyl acetate (50 mL×2). Dried with Na₂SO₄, the solvent was evaporated in vacuum. The resulting mixture was used for next step without further purification, together with THF (50 mL) and HCl (2.0 mol/L, 2.5 mL), were stirring at 60 °C for 1 h. The solvent was removed and the residue washed with water to afford an orange solid, which was purified by column chromatography (CH₂Cl₂/CH₃OH

= 50/1) to give the compound. (0.21 g, 65%) ^1H NMR (400 MHz, CDCl_3): 1.25 (t, $J = 7.2$ Hz, 6H), 3.83 (m, 4H), 8.04 (d, $J = 8.4$ Hz, 4H), 8.22 (d, $J = 8.4$ Hz, 4H), 10.10 (s, 2H).



Cycling tests

We studied the stability of FL-SNW-DPP-0.11 as a chemical sensor by the cycling test. Here we just take the quenching fluorescence of TNP for an example. 25 mg FL-SNW-DPP-0.11 was suspended in 25 mL THF in a volumetric flask and stirred overnight to form well-distributed suspension. Then, 2 mL suspension was taken out into a cuvette to make a fluorescent measurement. After the measurement, the suspension was carefully retrieved back to the volumetric flask, and 75 μL TNP solution (0.04 M) was added into the volumetric flask to make the concentration of TNP in the system as 120 μM . The volumetric flask was shaken to make sure the whole suspension mix well. Then, 2 mL suspension was taken out into a cuvette to measure its fluorescent spectra. That is the first cycling test. Afterward, the suspension was retrieved back again. The whole suspension was centrifuged, and the residual solid was washed successively with hot THF to remove the guest molecules of TNP completely. The regenerated FL-SNW-DPP-0.11 was suspended in 25 mL THF in the volumetric flask to repeat the second cycling test.

In the cycling test, it is important to make sure that the concentration of suspension used for conducting fluorescent spectrum was at the same level (2 mg / 2 mL), so we amplified the amount of sample in this procedure to reduce the experimental error.

2. Thermogravimetric analysis

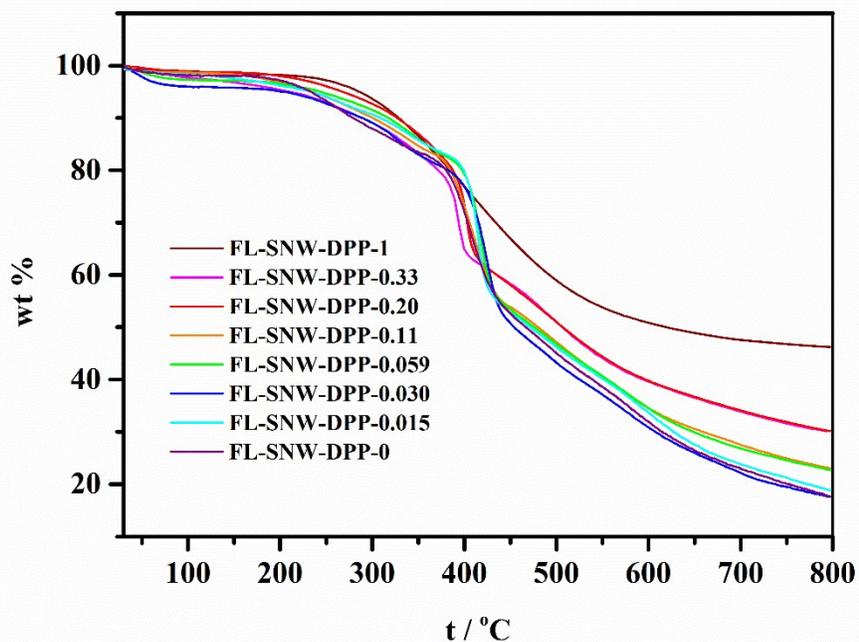


Fig. S1 Thermogravimetric curves of FL-SNW-DPPs.

3. Fourier transform infrared spectroscopy

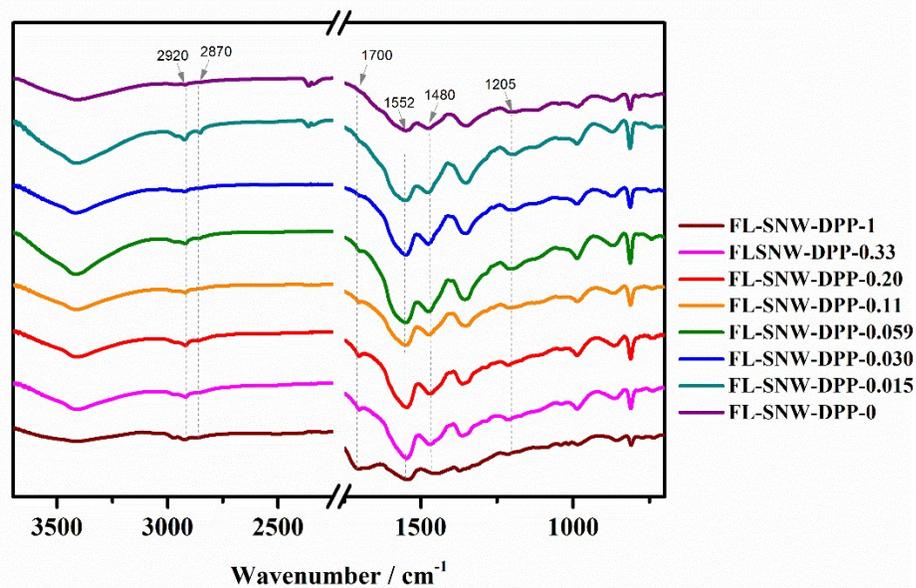


Fig. S2 Fourier Transform infrared spectroscopy of FL-SNW-DPPs.

4. UV-vis reflective spectra

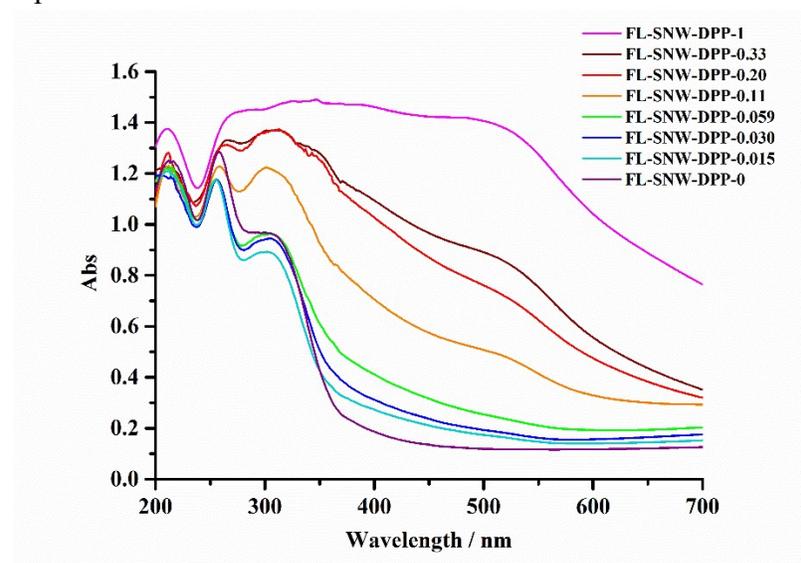


Fig. S3 UV-vis reflective spectra of FL-SNW-DPPs

5. Solid state ^{13}C NMR spectra

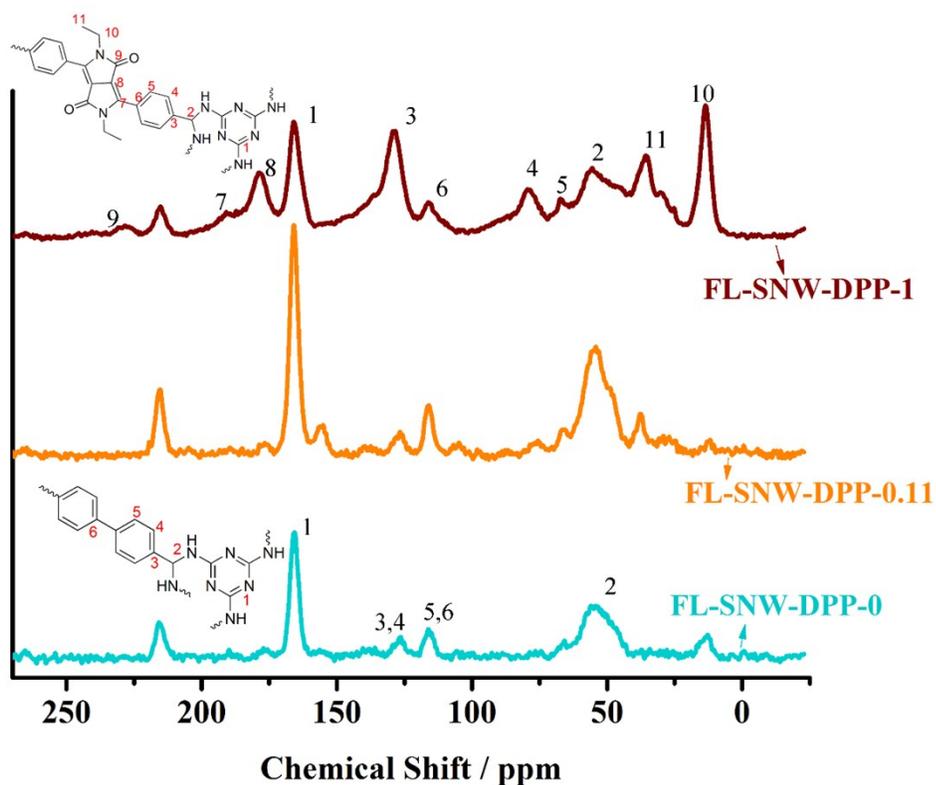


Fig. S4 Solid state ^{13}C NMR spectrum of FL-SNW-DPP-0, FL-SNW-DPP-0.11 and FL-SNW-DPP-1.

The signals at 129, 126, 117 and 115 ppm is attributed to the carbon atoms of biphenyl moieties. The existence of DPP moieties can be confirmed by the peaks at 228, 191, 179, 128, 116, 79, 67, 36 and 14ppm¹. The signal at 215 ppm corresponds to the terminal formyl group. The resonance at 55 ppm can be correlated to the tertiary carbon atoms of newly formed carbon-nitrogen double bond.

For FL-SNW-DPP-0.11, the fraction of DPP moieties is too low for detection. While for the network of FL-SNW-DPP-0.11, the melamine would be probably linked by either biphenyl moieties or DPP moieties. The chemical environment of the carbon atoms of melamine moieties would be versatile according to the various adjacent moieties, as a result, several resonances (176, 165 and 155 ppm) correspond to the carbon atoms of triazine rings. As a contrast, single signal (165 ppm) is attributed to those carbon atoms for FL-SNW-DPP-0 and FL-SNW-DPP-1.

6. Elemental analysis

Table S1 Elemental analysis results (C, H, N) of FL-SNW-DPPs

| | N% | C% | H% | N/C (mass ratio) |
|------------------|-------|-------|------|------------------|
| Fl-SNW-DPP-0 | 38.10 | 38.09 | 4.98 | 1.000263 |
| Fl-SNW-DPP-0.015 | 39.18 | 39.22 | 5.08 | 0.99898 |
| Fl-SNW-DPP-0.030 | 38.16 | 40.36 | 4.99 | 0.945491 |
| Fl-SNW-DPP-0.059 | 37.72 | 40.88 | 4.92 | 0.922701 |
| Fl-SNW-DPP-0.11 | 35.56 | 43.97 | 4.71 | 0.808733 |
| Fl-SNW-DPP-0.20 | 31.79 | 45.38 | 4.78 | 0.700529 |
| Fl-SNW-DPP-0.33 | 30.63 | 45.20 | 4.62 | 0.677655 |
| Fl-SNW-DPP-1 | 17.38 | 55.21 | 4.86 | 0.314798 |

To quantitatively measure the DPP content in the skeleton, we used elemental analysis to collect N and C content value. N/C mass ratio was calculated to determine the DPP density in the skeleton. For Fl-SNW-0, all formyl groups come from 4,4'-Biphenyldicarboxaldehyde. As the χ value increases, the 4,4'-Biphenyldicarboxaldehyde moieties are gradually replaced by 4,4'-(2,5-diethyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dibenzaldehyde. As a result, the absolute C content and N content are both in direct proportion to χ value. The N%/C% value can be described as the following equation.

$$N/C = \frac{a + cx}{b + dx}$$

In the equation, a , b , c and d are all constants while x represent the DPP density in the skeleton.

We used the measured N/C mass ratio values and χ values to fit the values of a , b , c and d . Fig S2 illustrates the experimental data and the fit of curves.

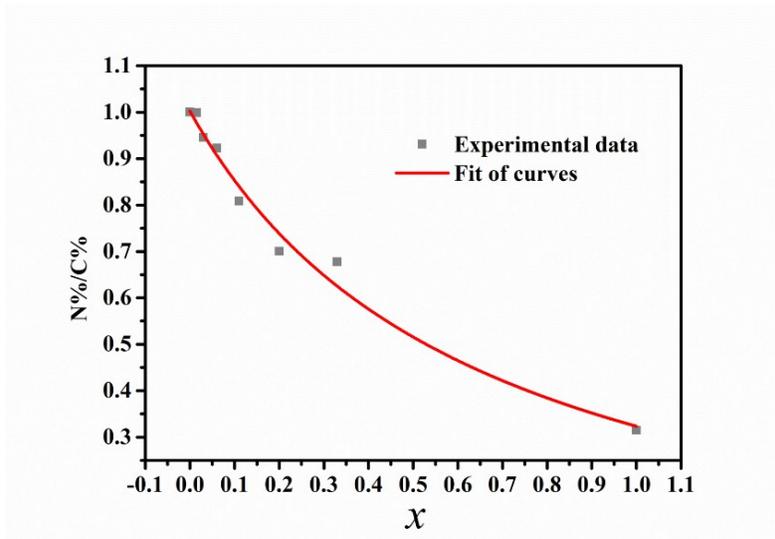


Fig. S5 Fitting plot of the functional relationship between N/C values and DPP density x .

Now we get the functional relationship between N/C mass ratio values and x . We can obtain the calculated density of DPP moieties x by substituting N/C mass ratio values into the function.

Table S2 χ values and calculated density of DPP moieties for FL-SNW-DPPs

| χ | 0 | 0.015 | 0.030 | 0.059 | 0.11 | 0.20 | 0.33 | 1 |
|------------------------|---|-------|-------|-------|------|------|------|------|
| calculated DPP density | 0 | 0.013 | 0.036 | 0.052 | 0.12 | 0.24 | 0.27 | 1.02 |

The calculated density of DPP moieties are in accordance of χ values, indicating that the DPP density in the skeleton is close to the feeding amount of DPP moieties, which is one of proofs for successful incorporation of DPP moieties in to the skeleton.

7. Solid-state fluorescent spectrum of FL-SNW-DPPs

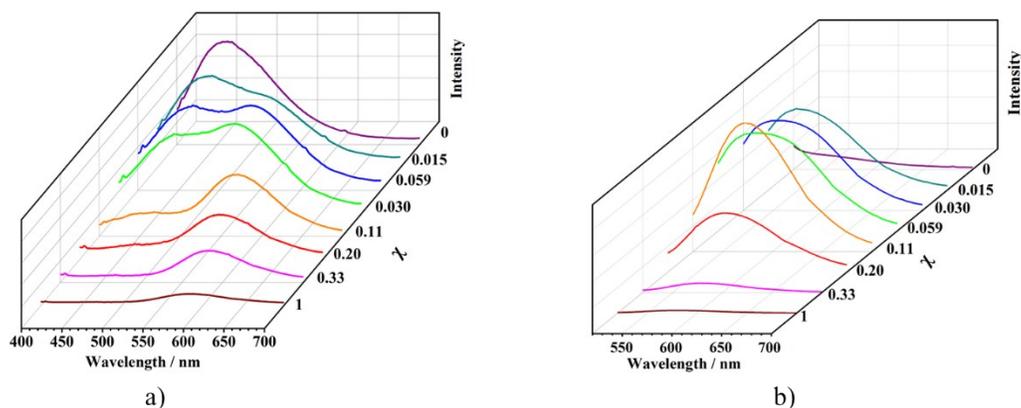


Fig. S6 Solid-state fluorescent spectrum of FL-SNW-DPP- χ excited at 370 nm (a) and 550 nm (b)

8. Nitrogen adsorption isotherms

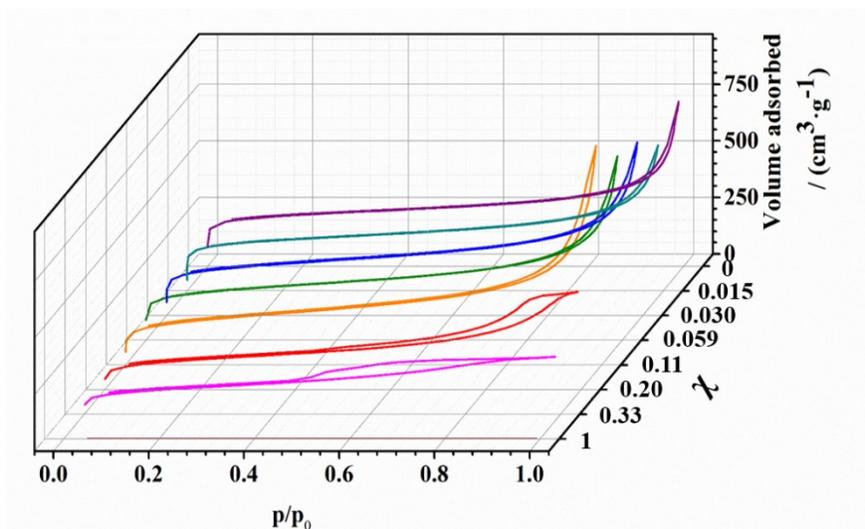


Fig. S7 Nitrogen adsorption isotherms measured under 77 K for FL-SNW-DPPs

9. Fluorescence quenching upon the addition of nitro aromatics and mechanism study

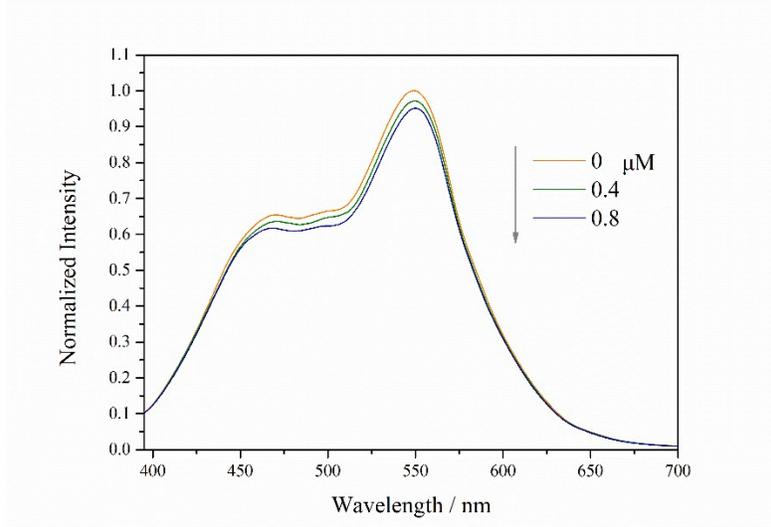


Fig. S8 Reduction of emission intensity of FL-SNW-DPP-0.11 in THF suspension upon addition of dilute TNP solution

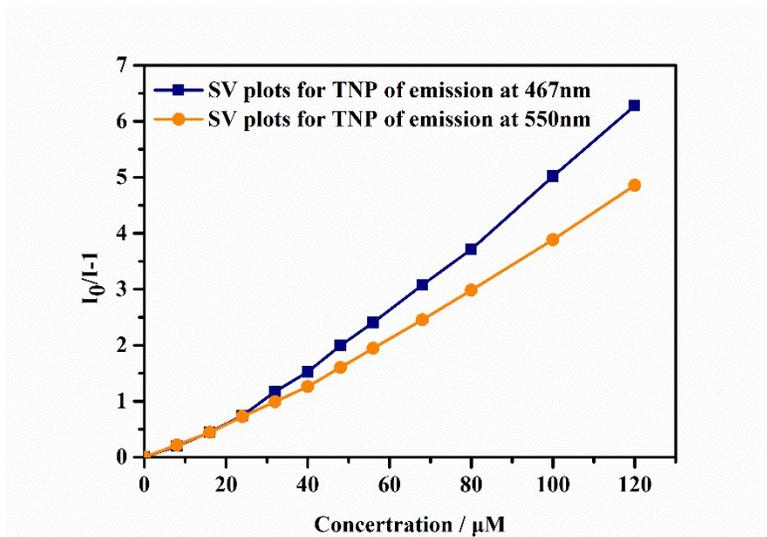


Fig. S9 SV plots for emission at 467 nm and 550 nm of FL-SNW-DPP-0.11 upon addition of TNP solution

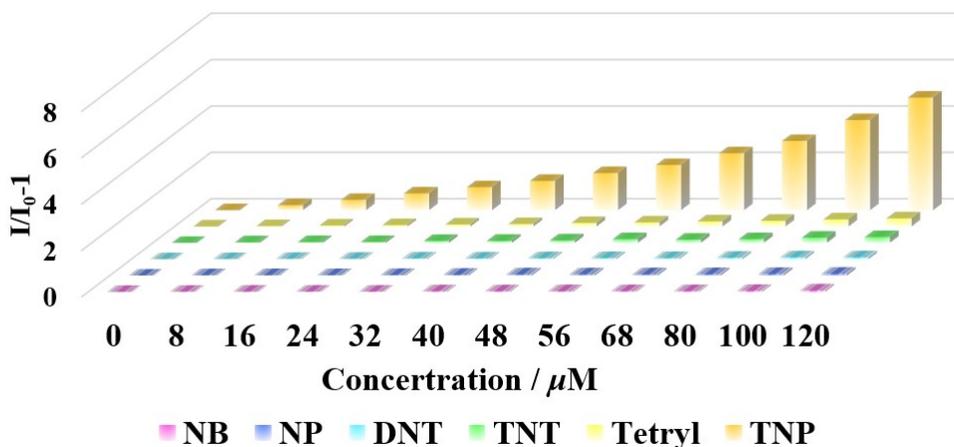


Fig. S10 SV plots for the emissions at 550 nm of FL-SNW-DPP-0.11 upon addition of various nitro aromatics solution.

The HOMO and LUMO orbital energies for FL-SNW-DPP- χ and analytes were calculated by density functional theory at the B3LYP/6-31G** level to illuminate the mechanism of fluorescence change and high selectivity for TNP. In the fluorescence titration experiments, both emissions at 467 nm and 550 nm show response to the addition of analytes, corresponding to two sub-structures of FL-SNW-DPP-0.11 (Fig. S7). The orbital energies of these two sub-structures were respectively calculated. A driving force for photo-induced electron transfer (PET) from

polymer to electron-deficient analytes is formed, attributing to the LUMO of both sub-structures of polymer lie a higher energy than LUMO of nitro aromatics, leading to the fluorescence quenching (Fig. S8). The LUMO energy of TNP is much lower than most of other nitro aromatics, such as NB, NP, DNT, and TNT, indicating an easier electron transfer process, which is in good agreement of excellent quenching efficiency for TNP. While the quenching efficiency of Tetryl is much lower than that of TNP, in spite of their similar LUMO energy, indicating that photo induced electron transfer is not the only mechanism for quenching. The nonlinear nature of SV plots for TNP suggest the probability of energy transfer process between TNP and FL-SNW-DPP-0.11. To confirm this mechanism, we conducted the adsorption spectrum of each nitro aromatic. Only the adsorption band of TNP exhibits significant overlap with the emission band of FL-SNW-DPP-0.11, indicating the larger probability of fluorescence resonance energy transfer (FRET) process between FL-SNW-DPP-0.11 and TNP. FRET, combined with PET process, amplify the quenching efficiency of TNP, hence the high selectivity.

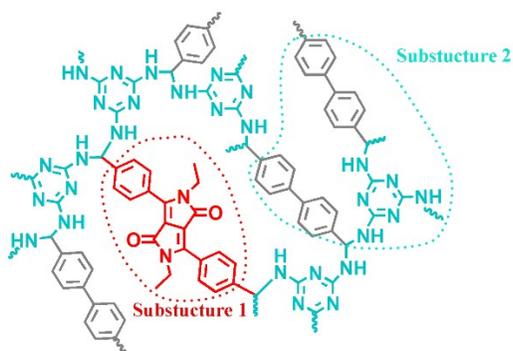


Fig. S11 Definition of substructure 1 and substructure 2

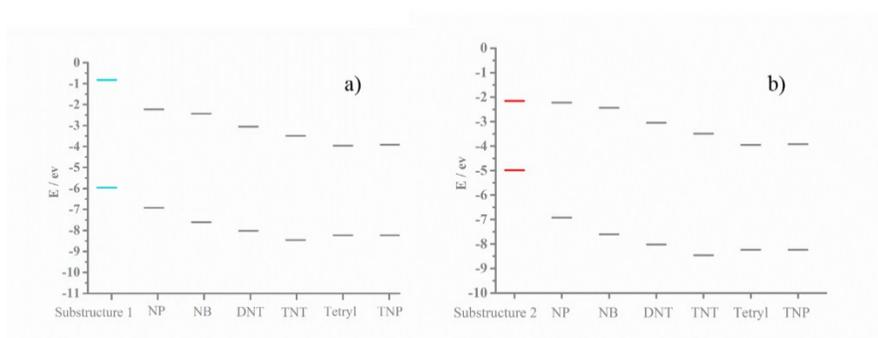


Fig. S12 HOMO and LUMO energy for substructure 1 (a), substructure 2 (b), compared with those of various nitro aromatics

Table S3 Calculated HOMO and LUMO energies for substructure 1 substructure 2 and nitro aromatics

| | HOMO energy / ev | LUMO energy / ev |
|----------------|---------------------|---------------------|
| Substructure 1 | -5.955 | -0.827 |
| Substructure 2 | -4.982 | -2.157 |
| NB | -7.601 | -2.434 |
| NP | -6.921 | -2.223 |
| Tetryl | -8.236 | -3.953 |
| DNT | -8.016 | -3.045 |
| TNT | -8.459 | -3.490 |
| TNP | -8.232 | -3.916 |

10. Fluorescence enhancement upon the addition of mesitylene and mechanism

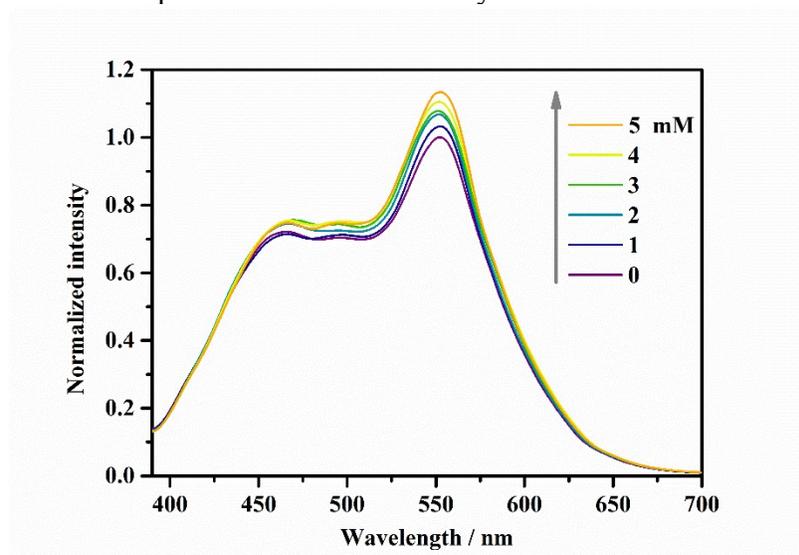


Fig. S13 Enhancement of emission intensity of FL-SNW-DPP-0.11 in THF suspension upon addition of Mesitylene solution

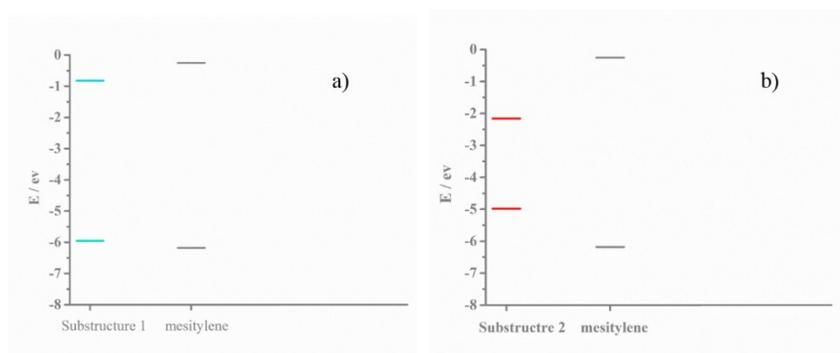


Fig. S14 HOMO and LUMO energy for substructure 1 (a), substructure 2 (b), compared with that of mesitylene

Table S4 Calculated HOMO and LUMO energies for substructure 1 substructure 2 and mesitylene

| | HOMO energy / ev | LUMO energy / ev |
|----------------|---------------------|---------------------|
| Substructure 1 | -5.955 | -0.827 |
| Substructure 2 | -4.982 | -2.157 |
| mesitylene | -6.180 | -0.255 |

11. Cycling tests

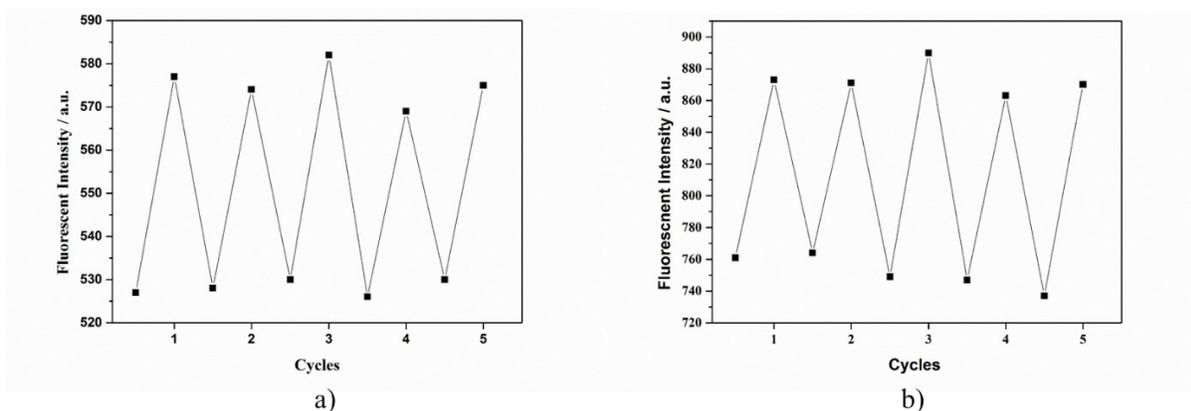


Fig. S15 Cycling tests of FL-SNW-DPP-0.11 upon the addition of mesitylene (5 mM).
Fluorescent intensity data of emission at 467 nm (a) and 550 nm (b)

References

- 1 G. Zhang, L. Song, S. Bi, Y. Wu, J. Yu and L. Wang, *Dyes and Pigments*, 2014, 102, 100.