

Supporting Information

A fluorescence sensing determination of 2, 4, 6-trinitrophenol based on cationic water-soluble pillar[6]arene graphene nanocomposite

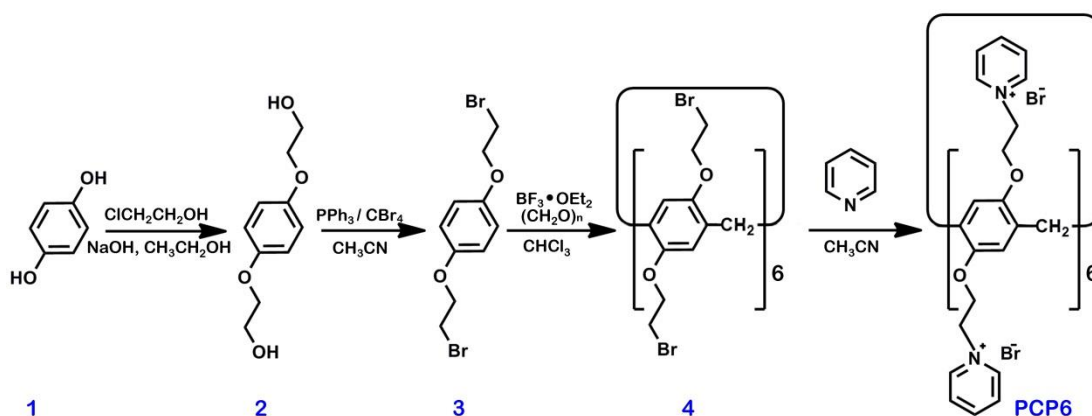
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S1. Reagents and methods

Hydroquinone, 1,2-dihydroxybenzene, boron trifluoride diethyl etherate, chloroform, carbon tetrabromide, triphenylphosphine, acetonitrile, paraformaldehyde, pyridine were reagent grade and used as received. Solvents were either employed as purchased or dried according to procedures described in the literature. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DMX-400 spectrometer at 400 MHz and 500 MHz. PCP6 [1-3] was synthesized according to the previous papers procedures.

S2. Synthesis of pyridine functionalized pillar[6]arene (PCP6)



Scheme S1. Synthetic route of PCP6.

Synthesis of 2: 50 mL of aqueous solution of NaOH (12.5 g, 311.2 mmol) was added to 150 mL of ethanol solution containing 1,2-dihydroxybenzene (HQ, 11.43 g, 104.0 mmol) under stirring for 25 min followed by addition of 2-chloroethanol (25.1 g, 311.7 mmol) under refluxing for 72 h. After that, the pH of the mixture solution was adjusted to 6–7, and the solvent was removed by reduced pressure distillation. Ethanol (120 mL) was added to dissolve the residual solid at the elevated temperature, and then the hot mixture solution was filtered to remove insoluble inorganic salts. The filtrate was concentrated to get the crude product. The pure product **2** was obtained by recrystallization in ethanol. The ^1H NMR spectrum of **2** is shown in Figure S1. ^1H NMR (400 MHz, D₂O, rt) δ (ppm): 6.925 (s, 4H), 4.028 (t, J = 4.4 Hz, 4H), 3.821 (t, J

= 4 Hz, 4H). The ^{13}C NMR spectrum of **2** is shown in Figure S2. ^{13}C NMR (100 MHz, D_2O , rt) δ (ppm): 152.72, 116.24, 70.08, 60.15.

Synthesis of 3: A solution of **2** (10.0 g, 50.4 mmol) and triphenylphosphine (32.0 g, 120 mmol) in dry acetonitrile (250 mL) was cooled with an ice bath. Under vigorous stirring, carbon tetrabromide (40.0 g, 120 mmol) was slowly added. The mixture was stirred at room temperature for 4 hours. Then cold water (250 mL) was added to the reaction mixture to give white precipitation. The precipitate was collected, washed with methanol/water (3:2, 3×100 mL), recrystallized from methanol, and dried under vacuum to afford **C2** as white crystals (14.4 g, 92%). The ^1H NMR spectrum of **3** is shown in Figure S3. ^1H NMR (400 MHz, CDCl_3 , rt) δ (ppm): 6.862 (s, 4H), 4.245 (t, $J = 6$ Hz, 4H), 3.616 (t, $J = 6.4$ Hz, 4H). The ^{13}C NMR spectrum of **3** is shown in Figure S4. ^{13}C NMR (100 MHz, CDCl_3 , rt) δ (ppm): 152.8, 116.06, 68.68, 29.28.

Synthesis of 4: Boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$, 3.26 g, 23.0 mmol) was added to the mixed solution of paraformaldehyde (0.7 g, 23.0 mmol) and **3** (3.37 g, 11.5 mmol) in chloroform (200 mL) under nitrogen atmosphere. Then the mixture was stirred at room temperature for 3 hour. A green solution was obtained. The reaction mixture was then washed with water (3×120 mL) and dried with excess Na_2SO_4 . After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:2 v/v) as the eluent to get a white powder of **4** (0.52 g, 15 %). The ^1H NMR spectrum of **4** is shown in Figure S5. ^1H NMR (500 MHz, CDCl_3 , rt) δ (ppm): 6.777 (s, 12H), 4.16 (t, $J = 6$ Hz, 24H), 3.867 (s, 12H), 3.545 (t, $J = 6$ Hz, 24H). The ^{13}C NMR spectrum of **C3** is shown in Figure S6. ^{13}C NMR (100 MHz, CDCl_3 , rt) δ (ppm): 150.16, 128.51, 115.83, 68.95, 30.63, 30.32.

Synthesis of PCP6: An excess amount of pyridine (2.4 g, 30 mmol) was added to a solution of **4** (1.5 g, 0.74 mmol) in CH_3CN (50 mL), and the resulting mixture was refluxed for 30 hours. After cooling to room temperature, the precipitate was filtered, and was washed by CH_3CN and dried to give a light yellow solid **PCP6**. The ^1H NMR spectrum of **PCP6** is shown in Figure S7. ^1H NMR (500 MHz, $\text{DMSO}-d_6$, rt) δ (ppm): 9.307 (s, 24H), 8.574 (t, $J=7.5$ Hz, 12H), 8.057 (s, 24H), 6.549 (s, 12H), 5.145

(s, 24H), 4.474 (s, 24H), 3.328 (s, 12H). The ^{13}C NMR spectrum of **PCP6** is shown in Figure S8. ^{13}C NMR (125 MHz, DMSO-*d*₆, rt) δ (ppm): 149.29, 145.91, 145.15, 127.66, 127.39, 115.30, 67.38, 60.09.

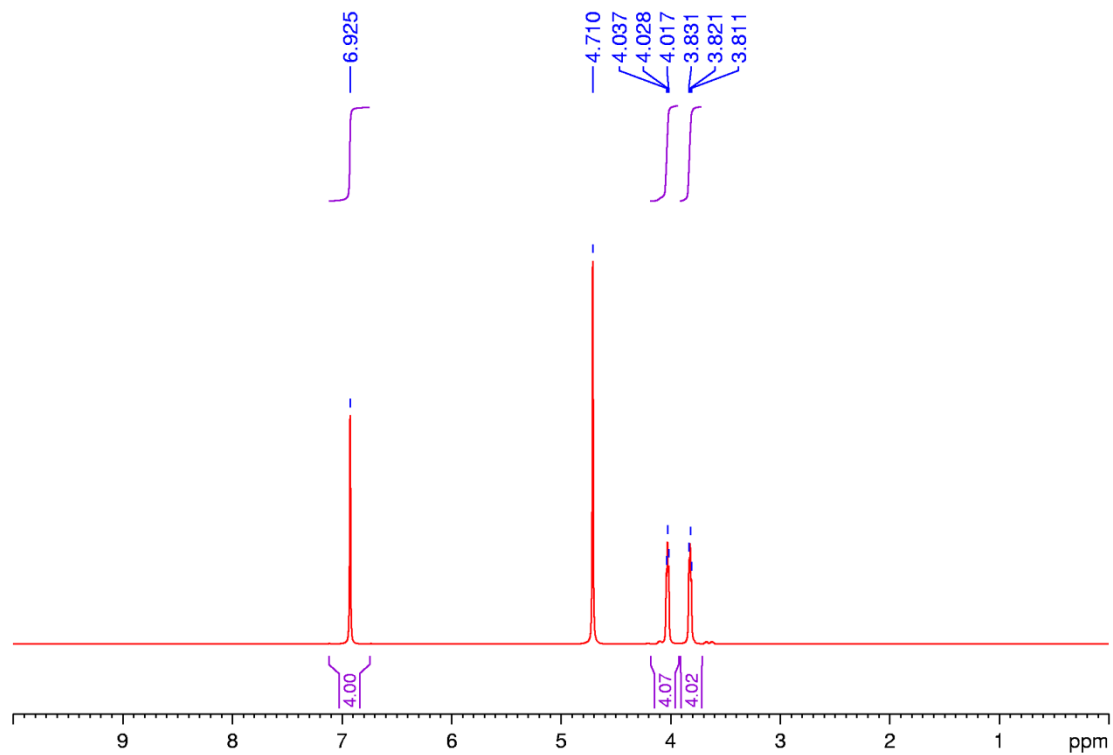


Figure S1. ¹H NMR spectrum (400 MHz, D₂O, 298 K) of **2**.

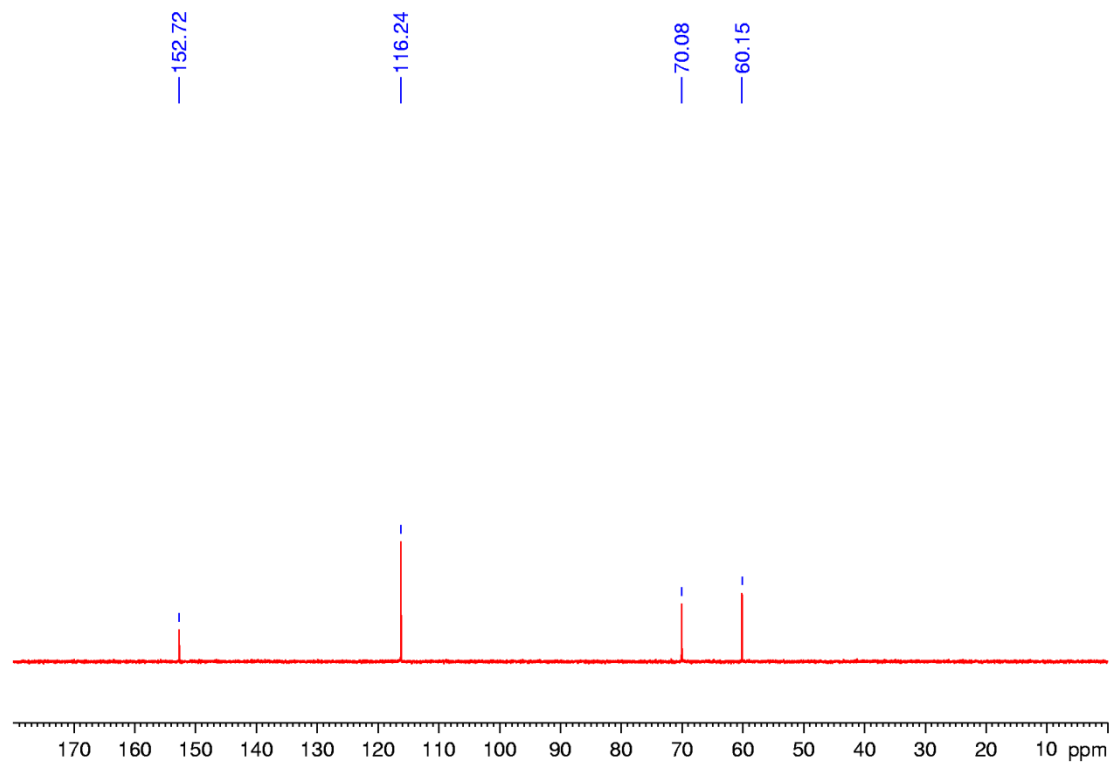


Figure S2. ¹³C NMR spectrum (100 MHz, D₂O, 298 K) of **2**.

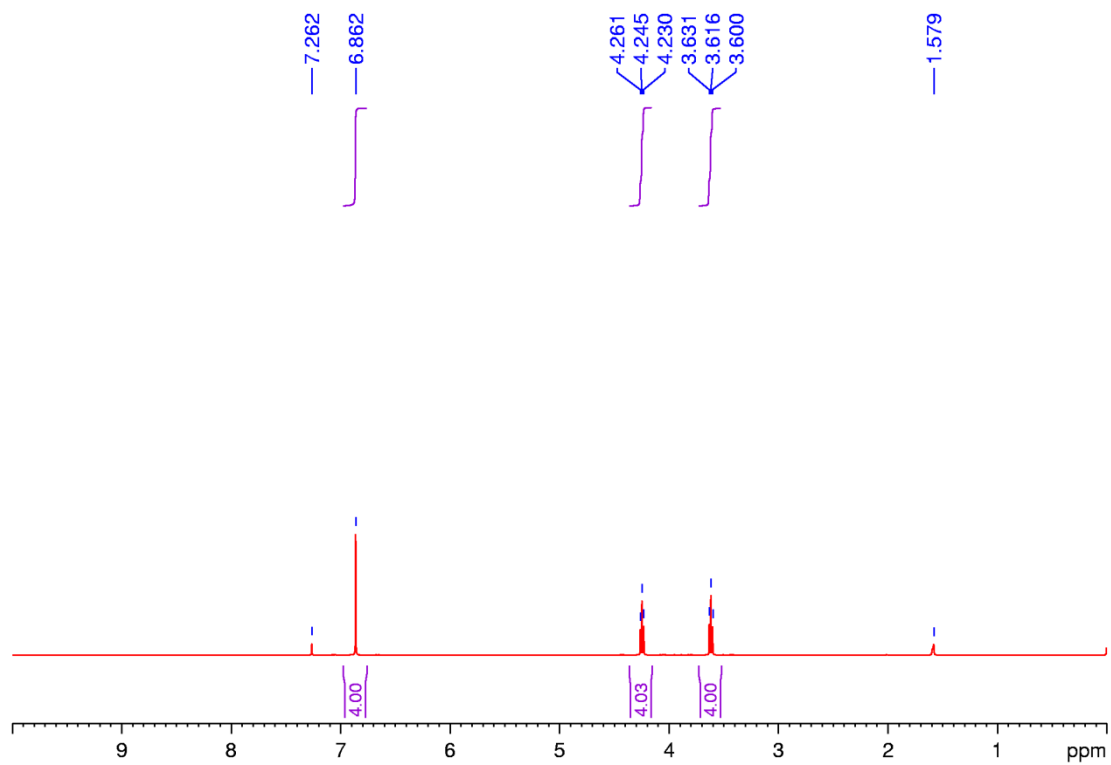


Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃, 298 K) of **3**.

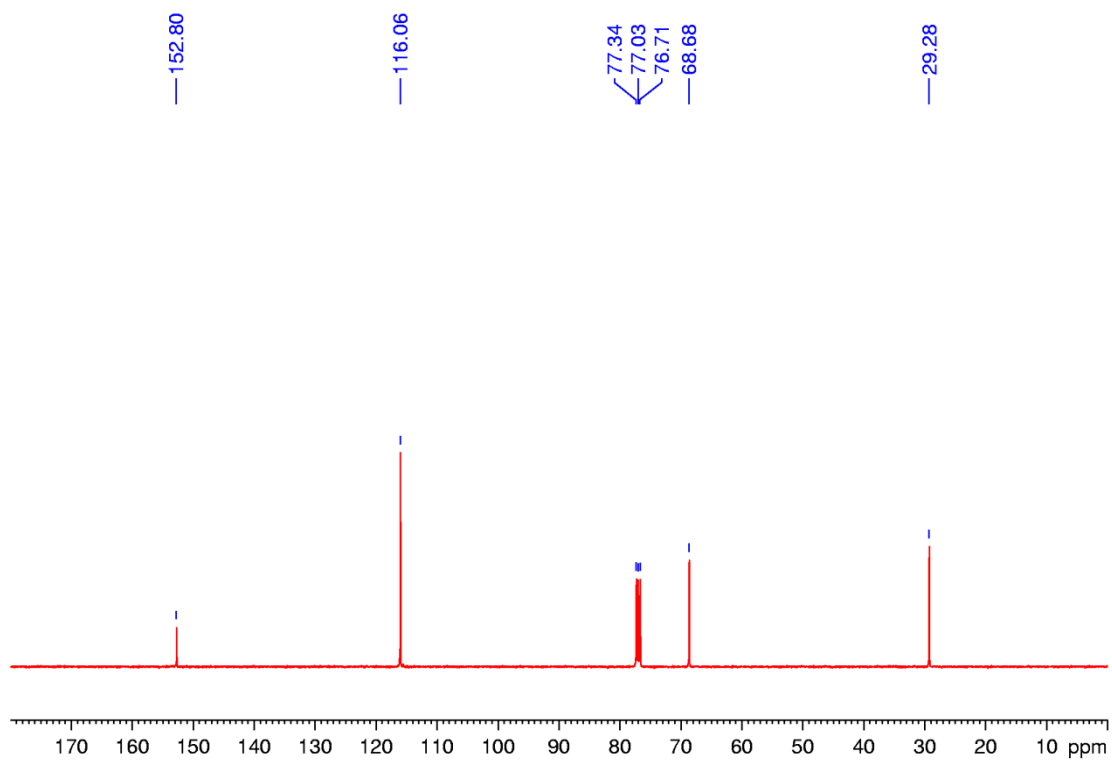


Figure S4. ¹³C NMR spectrum (100 MHz, CDCl₃, 298 K) of **3**.

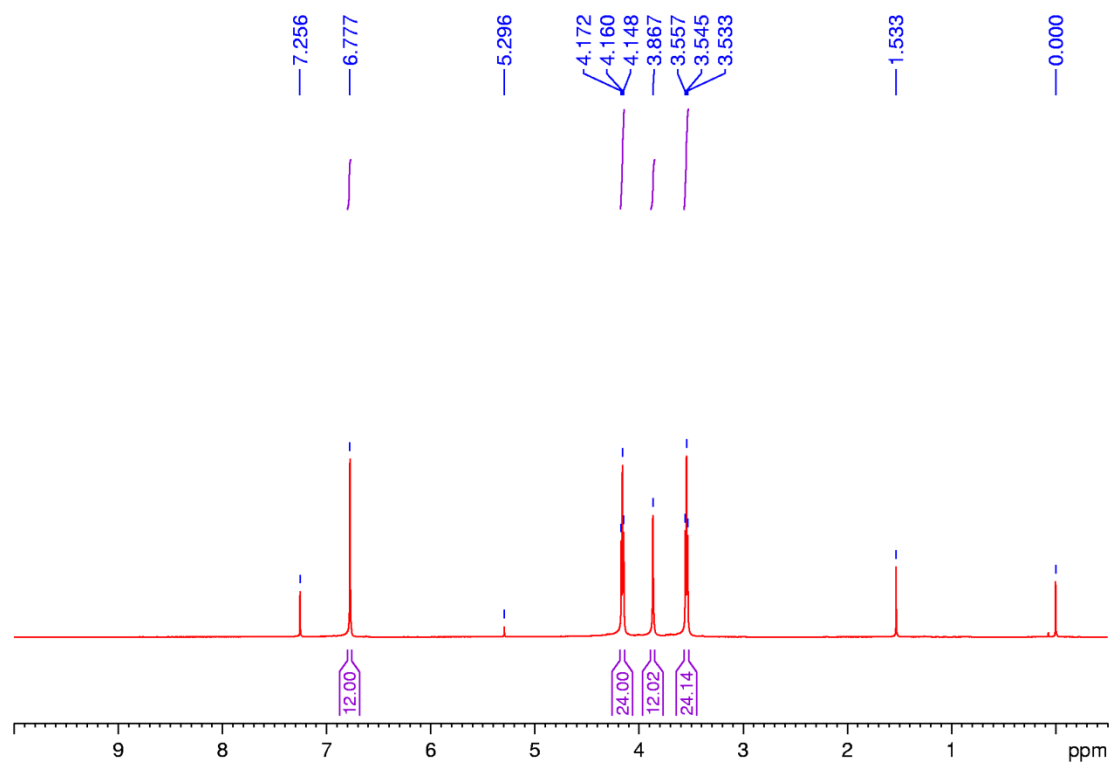


Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **4**.

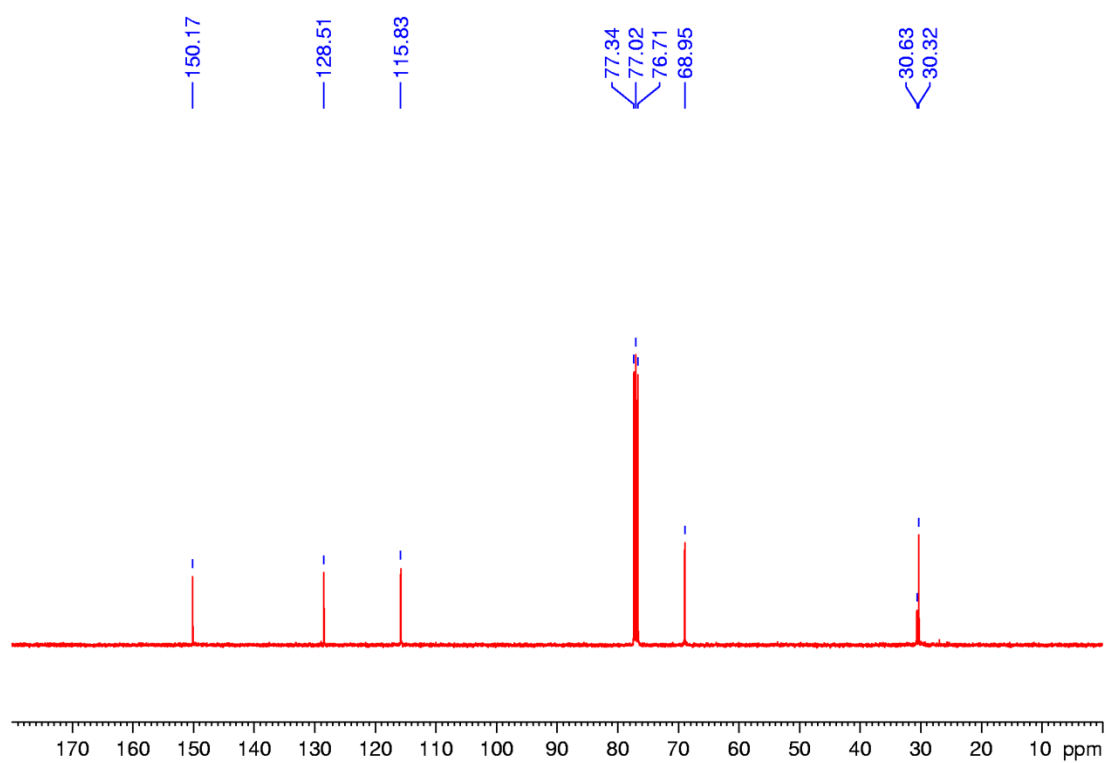


Figure S6. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) of **4**.

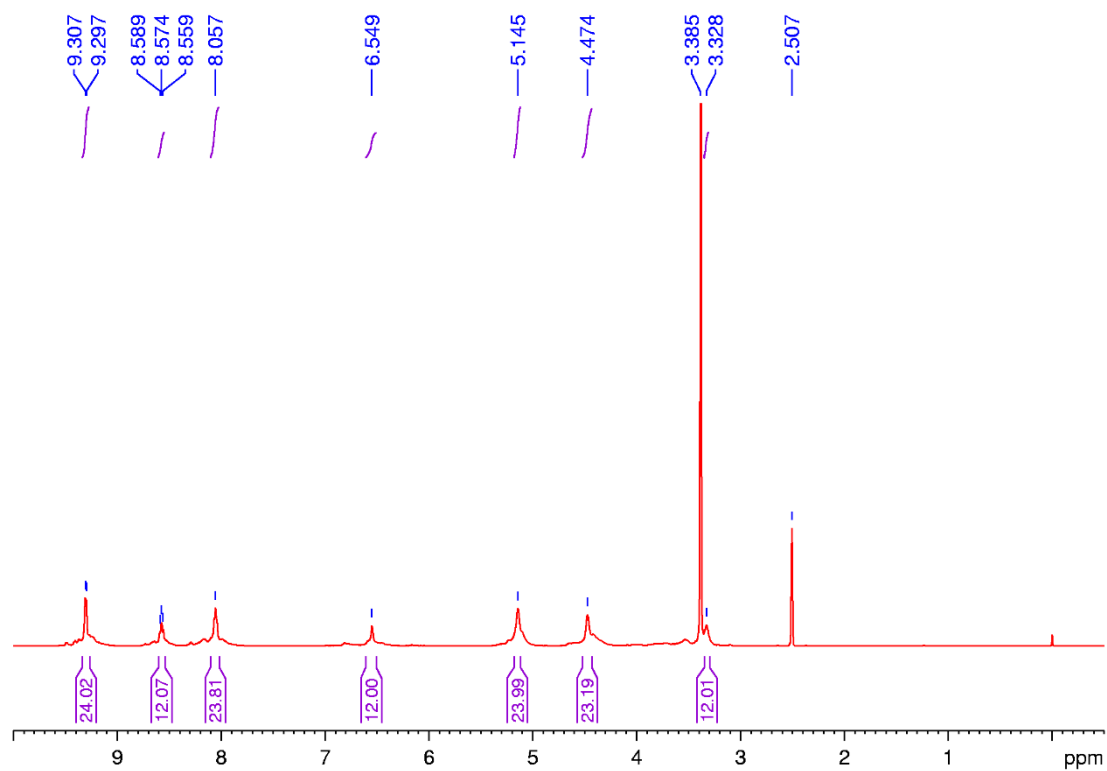


Figure S7. ^1H NMR spectrum (500 MHz, $\text{DMSO-}d_6$, 298 K) of **PCP6**.

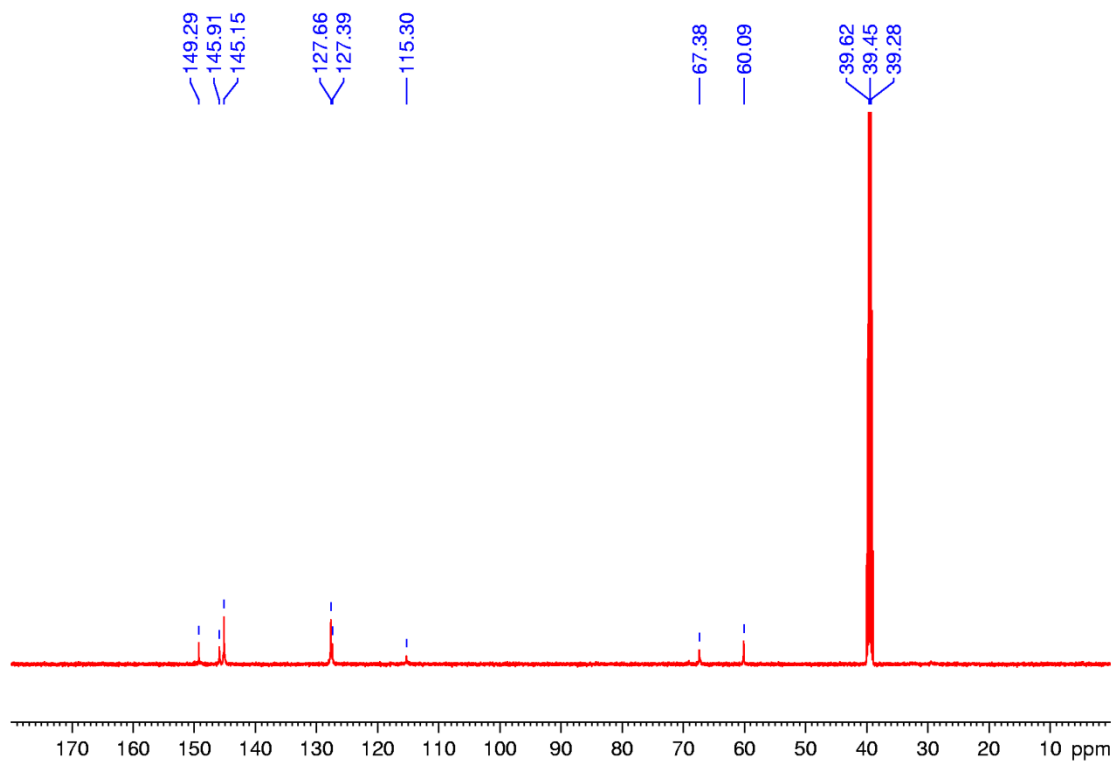


Figure S8. ^{13}C NMR spectrum (125 MHz, $\text{DMSO-}d_6$, 298 K) of **PCP6**.

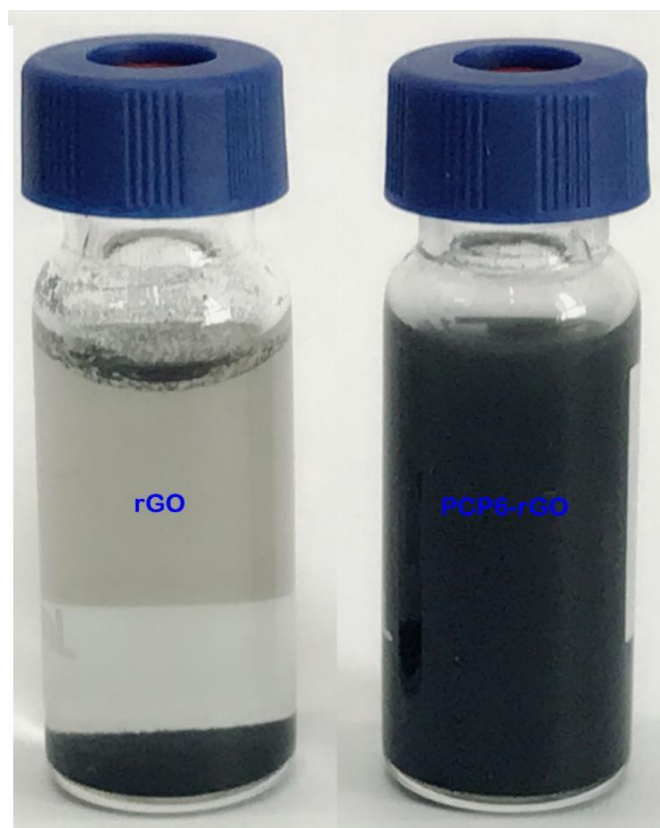


Figure S9. The photographs of rGO, PCP6-rGO aqueous dispersion.

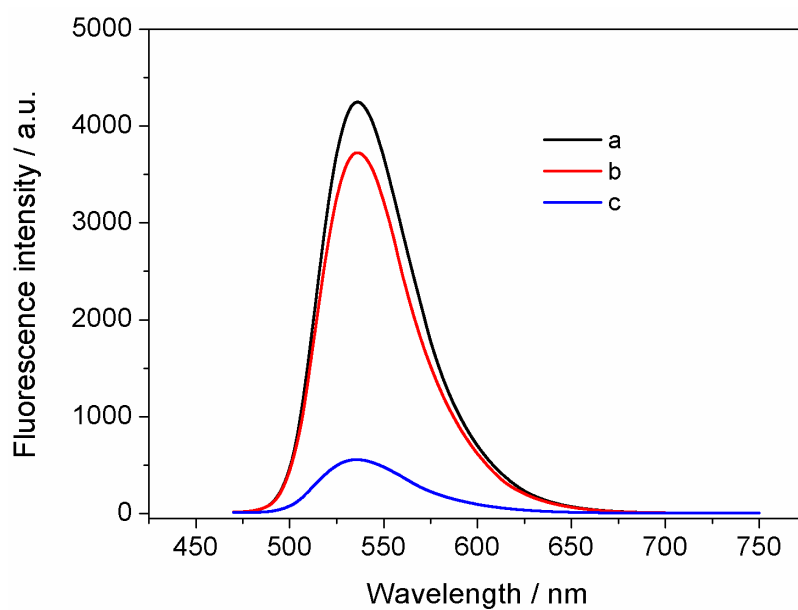


Figure S10. Fluorescence spectra of 10 μM AO (a), 10 μM AO in the presence of 20 μM PCP6 (b), and 10 μM AO in the presence of 18 $\mu\text{g mL}^{-1}$ PCP6-rGO (c).

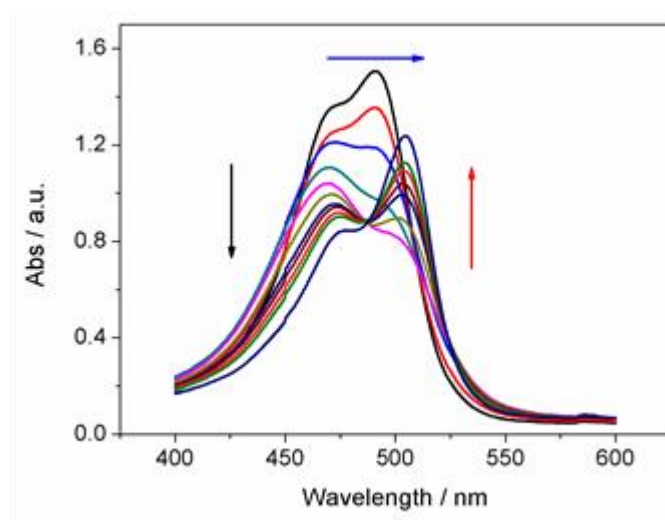


Figure S11. UV-vis spectra of 10 μM AO in the presence of 0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, and 50.0 μM of PCP6 in PBS (pH = 7.2).

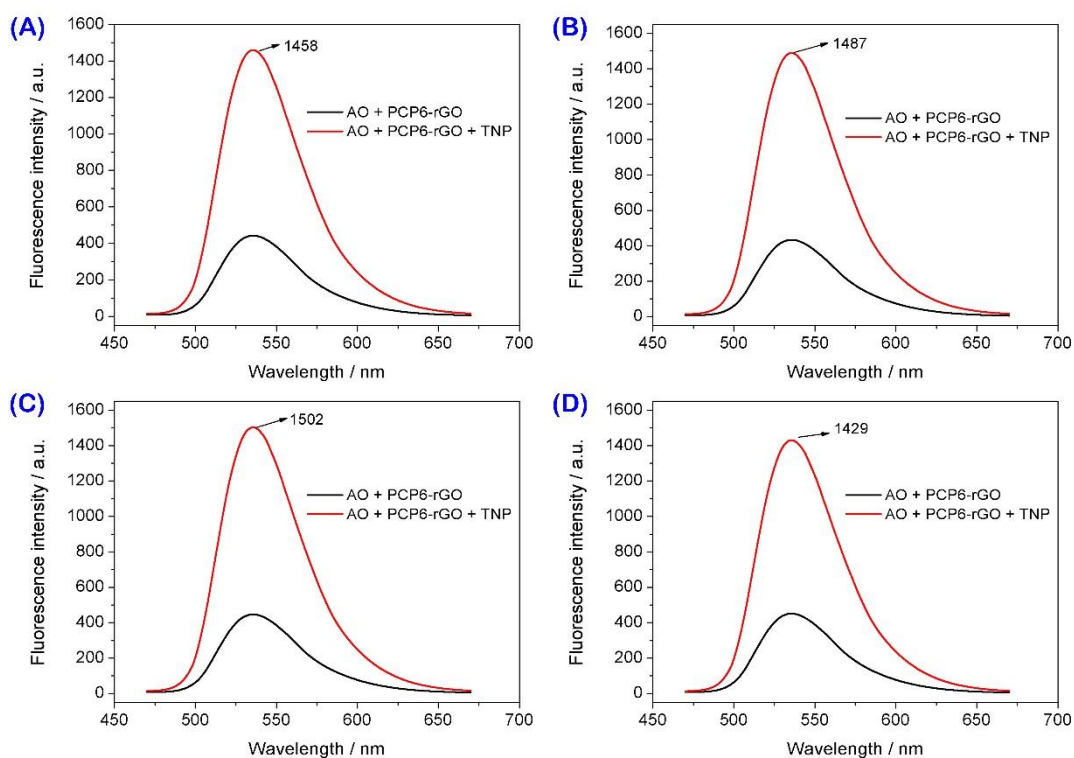


Figure S12. The effect of different temperatures on the recovering performance of TNP towards AO@PCP6-rGO; the same concentration of TNP with 20 μM and the temperature at 25 (A), 35 (B), 45 (C), and 50 $^{\circ}\text{C}$ (D), respectively.

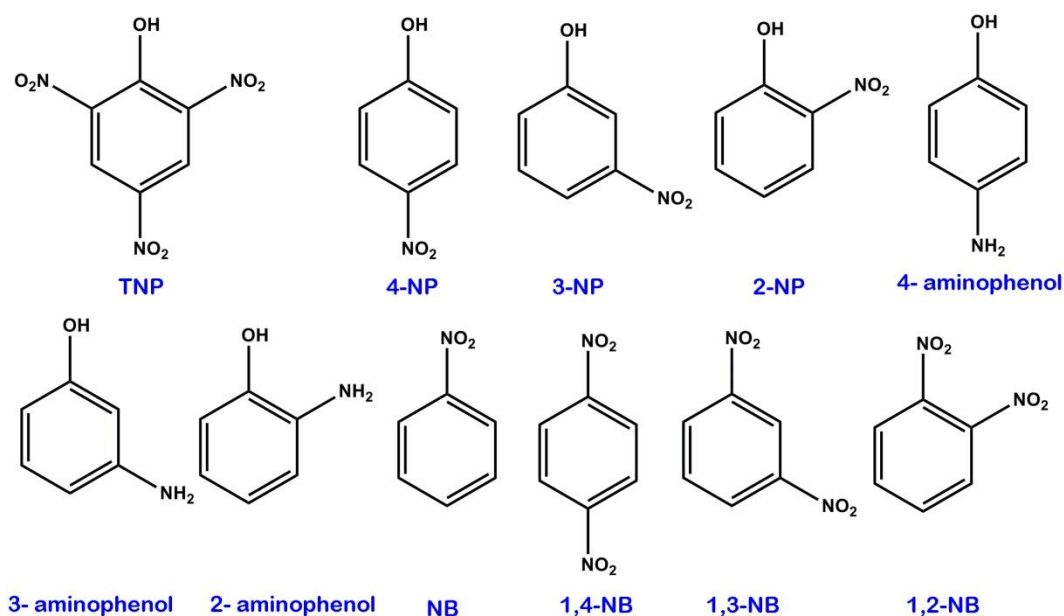


Figure S13. The chemical structures of TNP, 4-NP, 3-NP, 2-NP, 4-aminophenol, 3-aminophenol, 2-aminophenol, NB, 1,4-NB, 1,3-NB and 1,2-NB, respectively.

Table S1 Comparison of different methods for quantitative detection of TNP.

Electrode or matrix	Method	Liner range (μM)	LOD (μM)	Ref
Tb-CDs	Fluorescence	0.5–100	0.2	[4]
Ag nanoclusters	Fluorescence	0.1-20	0.1	[5]
GQDs	Fluorescence	0.1-15	0.09	[6]
MoS ₂ -QDs	Fluorescence	0.099-36.5	0.095	[7]
BNQDs	Fluorescence	0.25-200	0.14	[8]
N-GQDs	Fluorescence	1-60	0.3	[9]
Cu-BTC/ERGO/GCE	DPV	0.2-10	0.1	[10]
PCP6-rGO	Fluorescence	0.01-125	0.0035	This work

Reference

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