Supporting Information for

Neutral branched platinum-acetylide complex possessing a tetraphenylethylene core: preparation of luminescent organometallic gelator and its unexpected spectroscopic behaviour during sol-to-gel transition

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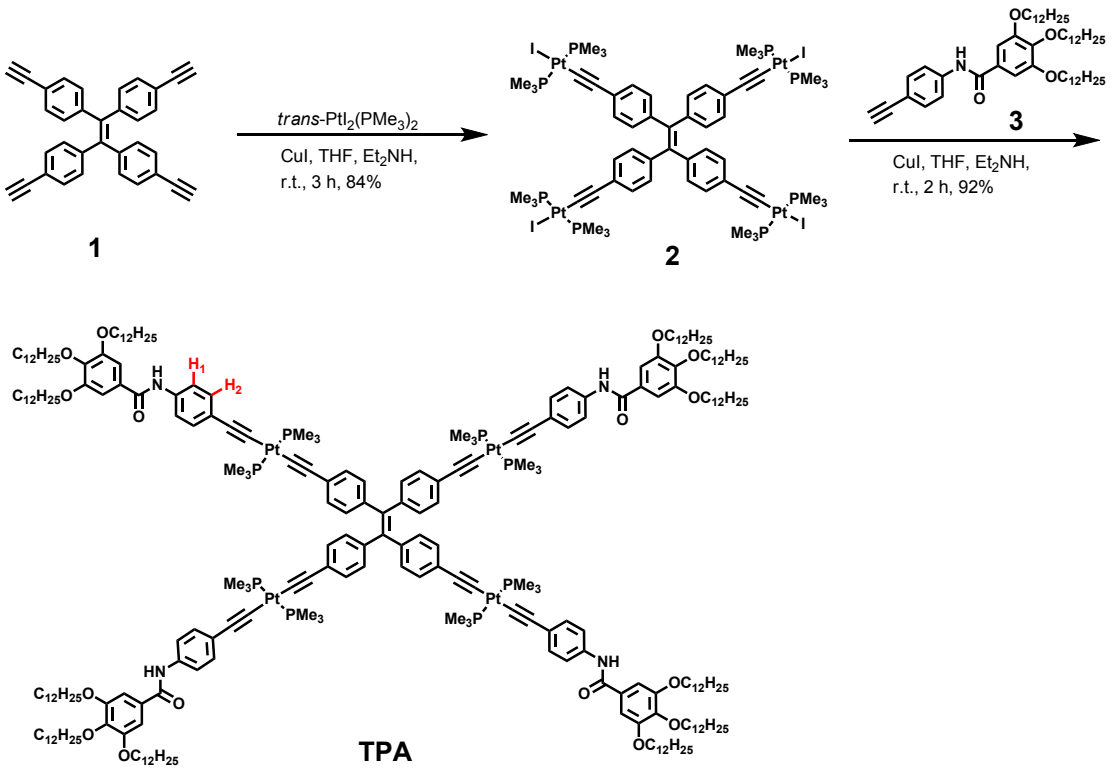
Contents:

1. General information

All reagents were analytical reagents and used without further treatment. THF used were dried according to standard procedures and degassed under N_2 for 30 minutes. Column chromatography was conducted by using silica-gel column .

^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz Spectrometer (^{1}H: 400 MHz; ^{31}P: 161.9 MHz; ^{13}C: 100 MHZ) at 298 K. The ^{1}H and ^{13}C NMR chemical shifts were reported relative to residual solvent signals, and ^{31}P NMR resonances were referenced to an internal standard sample of 85% H_3PO_4 (δ 0.0). Coupling constants (*J*) were denoted in Hz and chemical shifts (δ) in ppm. Multiplicities were denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. Fluorescence spectra were recorded on Varian Cary Eclipse.

2. The synthesis of complex TPA



Scheme S1 The synthesis of complex **TPA**.

Compound **2**: A solution of *trans*-$PtI_2(PMe_3)_2$ (639 mg, 1.02 mmol) and CuI (4 mg, 10 mol%) in a mixture of THF/Et_2NH (40 mL THF and 45 mL Et_2NH) was stirred at room temperature. Then compound **1** (91 mg, 0.21 mmol) dissolved in THF was added dropwise to the reaction mixture under an atmosphere of nitrogen. The reaction was stirred at room temperature for 3 hours. The solvent was then removed in vacuo, the resulting residue was separated by column chromatography on silica gel and the yellow solid **2** was obtained (417 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz,): δ 7.02-7.04 (m, 9H), 6.85-6.83 (m, 9H), 1.80-1.78 ppm (m, 72H). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ = -22.49 (s, $J_{Pt\text{-}P}$ = 1128.44 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.31, 139.98, 131.17, 130.10, 125.57, 99.77, 91.14, 90.99, 16.47, 16.26, 16.06, 15.86, 15.67. MALDI-MS: calcd for $[M + H]^+$: 2320.96, found: 2320.08. HRMS (ESI): calcd for $[M + 2Na]^{2+}$: 1182.9666, found: 1182.9639.

Compound **TPA**: A solution of compound **2** (150mg, 0.07 mmol) and CuI (2 mg, 10 mol%) in a mixture of THF/Et_2NH (10 mL THF and 10

mL Et_2NH) was stirred at room temperature. Then compound **3** (200 mg, 0.07 mmol) dissolved in THF was added dropwise to the reaction mixture under an atmosphere of nitrogen. The reaction was stirred at room temperature for 2 hours. The solvent was then removed in vacuo, the resulting residue was separated by column chromatography on silica gel and the yellow solid **TPA** was obtained (266 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz,): δ 7.63 (s, 4H), 7.48 (d, J = 8.4 Hz 8H), 7.20 (d, J = 7.6 Hz 8H), 7.02 (br, 17H), 6.84-6.82 (m, 8H), 4.03-4.01 (m, 24H), 1.80-1.78 (m, 96H), 1.47 (br, 24H), 1.26 (m, 216H), 0.90-0.86 (m, 36H). ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ = -20.21 (s, $J_{Pt\text{-}P}$ = 1148 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.38, 153.12, 141.46, 135.50, 131.65, 131.21, 130.48, 129.95, 119.72, 105.80, 73.51, 69.43, 31.88, 30.28, 29.61, 29.34, 26.04, 22.64, 15.60, 15.40, 15.21, 14.00. MALDI-MS: calcd for $[M + H]^+$: 4905.84, found: 4905.80.

3. The AIEE behavior of complex 2 in CH_2Cl_2/*n*-hexane

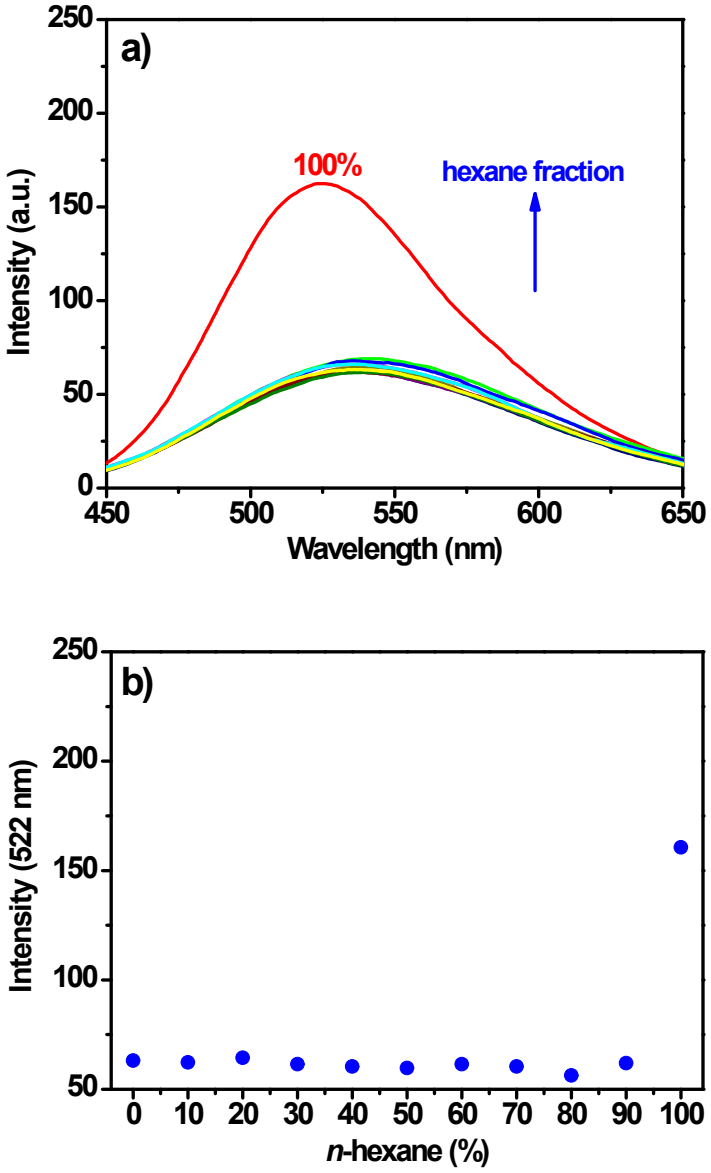


Fig. S1 Fluorescence spectra (a) and fluorescence intensity at 522 nm (b) of complex **2** in the CH_2Cl_2/*n*-hexane mixtures with different *n*-hexane fractions.

4. Fluorescence spectra of complexes 2 and TPA in CH_2Cl_2 and *n*-

hexane

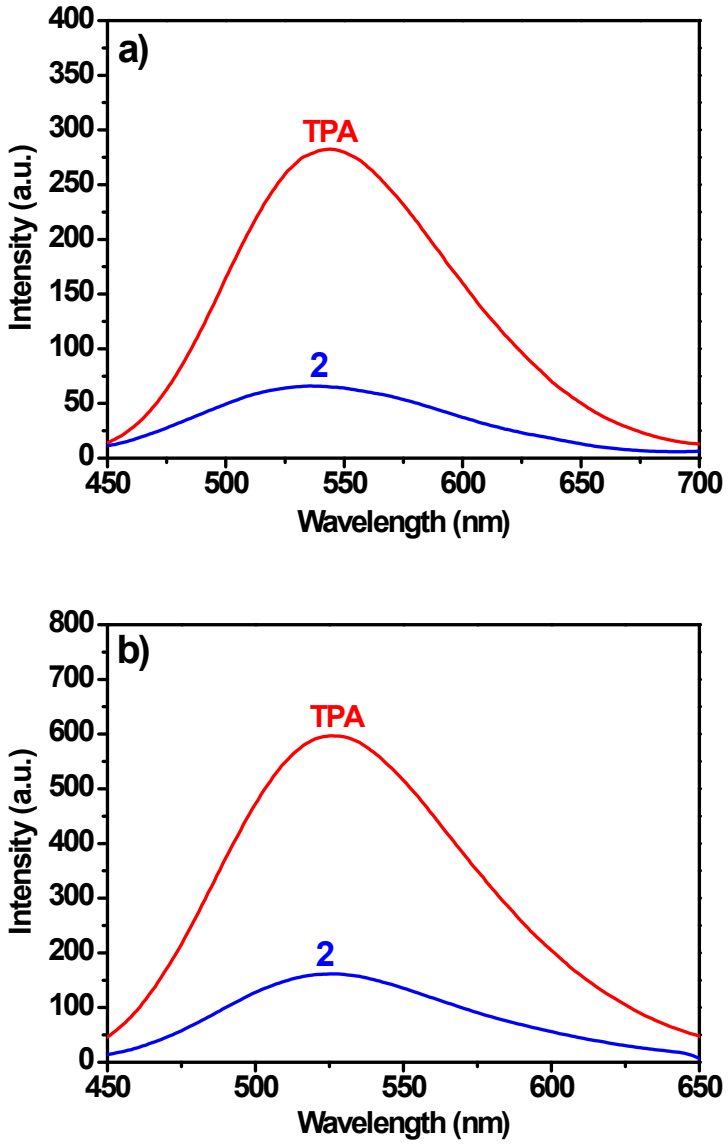


Fig. S2 Fluorescence spectra of complexes **2** and **TPA** in CH_2Cl_2 (a) and *n*-hexane (b).

5. SEM images of xerogel of TPA

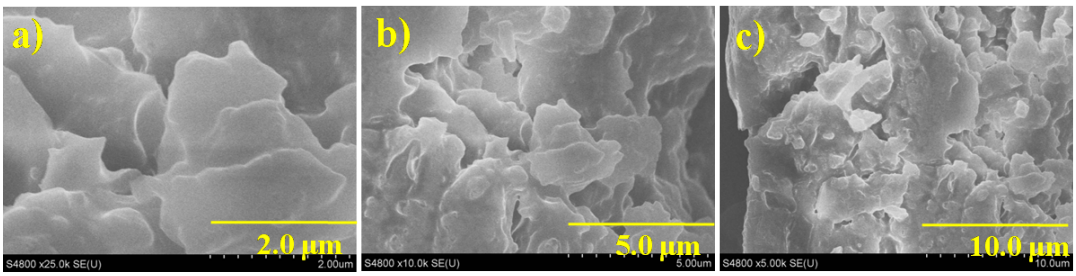


Fig. S3 SEM images of xerogel of **TPA** in ethyl acetate.

6. Concentration-dependent ^{1}H NMR spectra of TPA

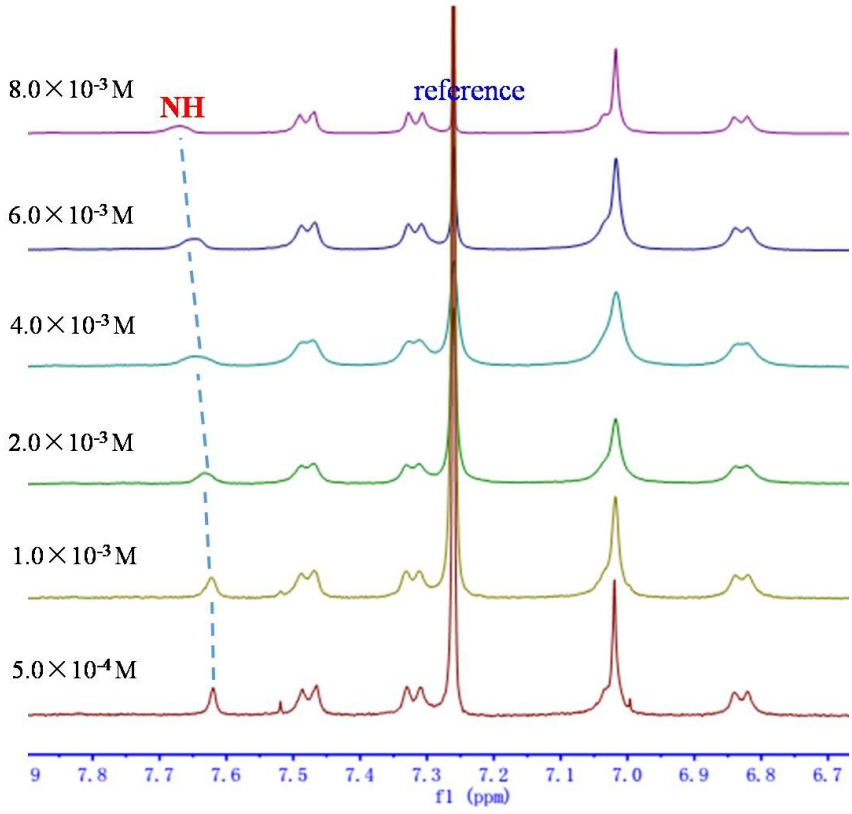


Fig. S4 The ^{1}H NMR spectra of **TPA** in $CDCl_3$ with different concentrations.

7. Temperature-depended emission spectra of TPA

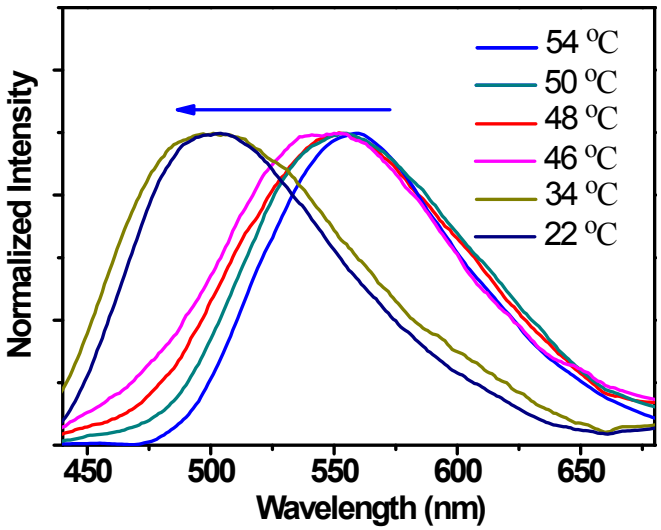


Fig. S5 The emission spectra of **TPA** in ethyl acetate with different temperatures.

8. The emission spectra of TPA in different solvents

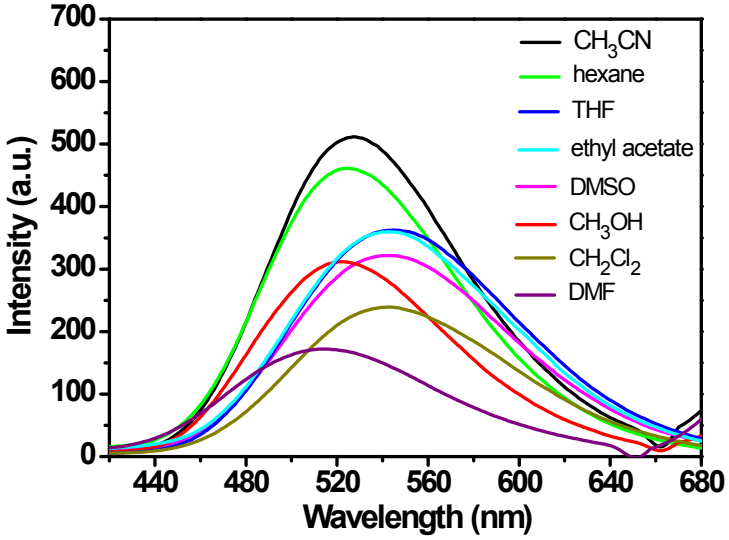


Fig. S6 The emission spectra of **TPA** in different solvents such as hexane, toluene, dichloromethane, tetrahydrofuran, ethyl acetate, acetonitrile, methanol, and dimethyl sulfoxide.

9. The normalized absorption spectra of TPA in CH_2Cl_2/*n*-hexane

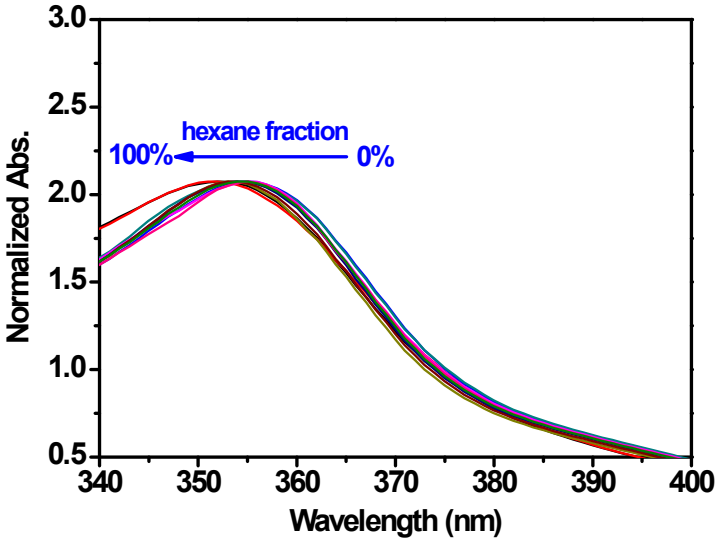
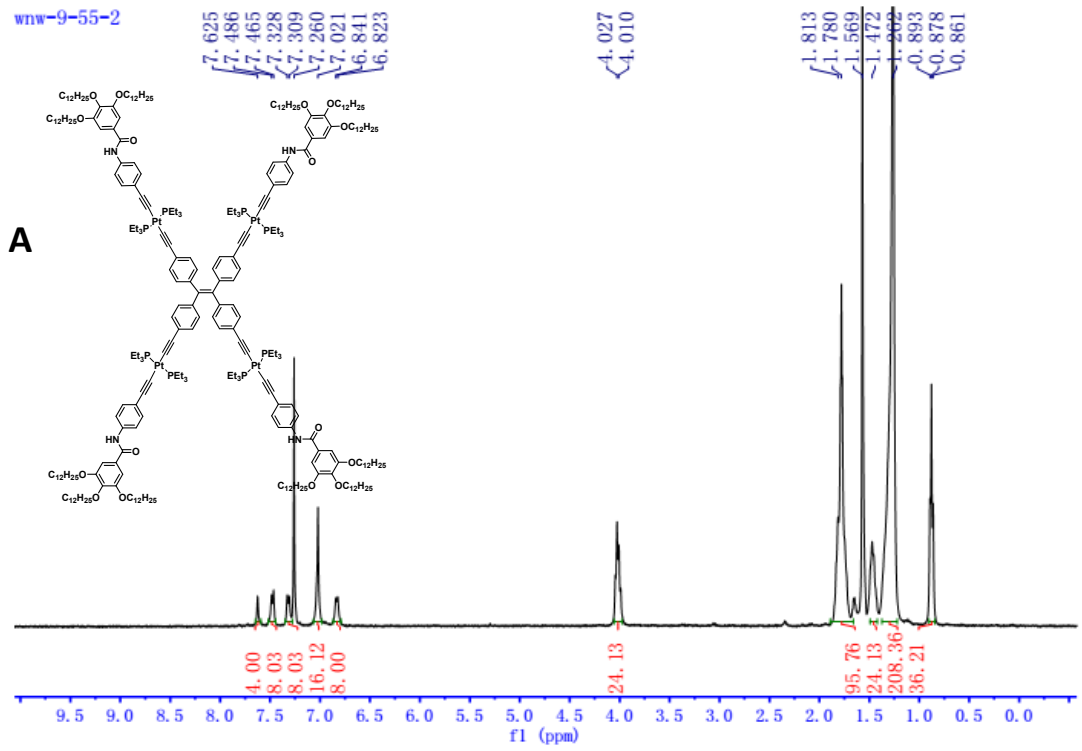


Fig. S7 The normalized absorption spectra of **TPA** in the CH_2Cl_2/*n*-hexane mixtures with different *n*-hexane fractions.

10. The ^{1}H, ^{31}P, and ^{13}C NMR spectra of TPA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7.625
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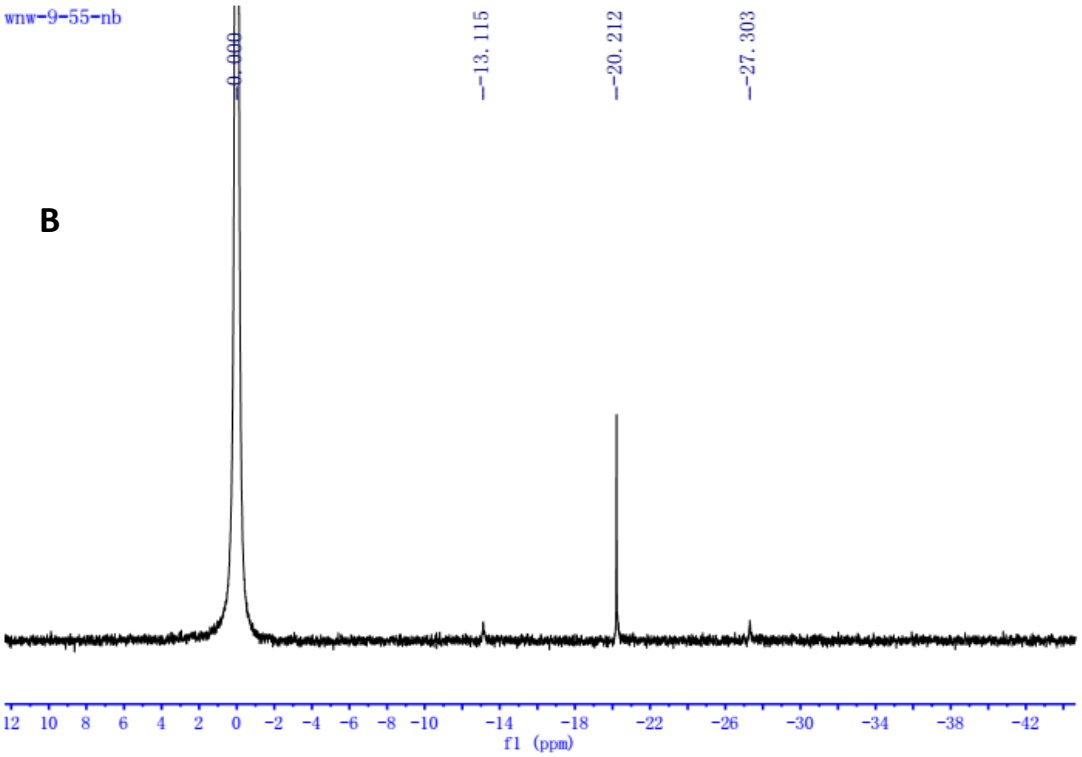
7.465
7.328
7.309
7.260
7.021
6.841
6.823
4.027
4.010
1.813
1.780
1.569
1.472
0.893
0.878
0.861
4.00
8.03
8.03
16.12
8.00
24.13
95.76
24.13
208.36
36.21
f1 (ppm)


wnw-9-55-nb
B
0.000
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-20.212
-27.303
f1 (ppm)

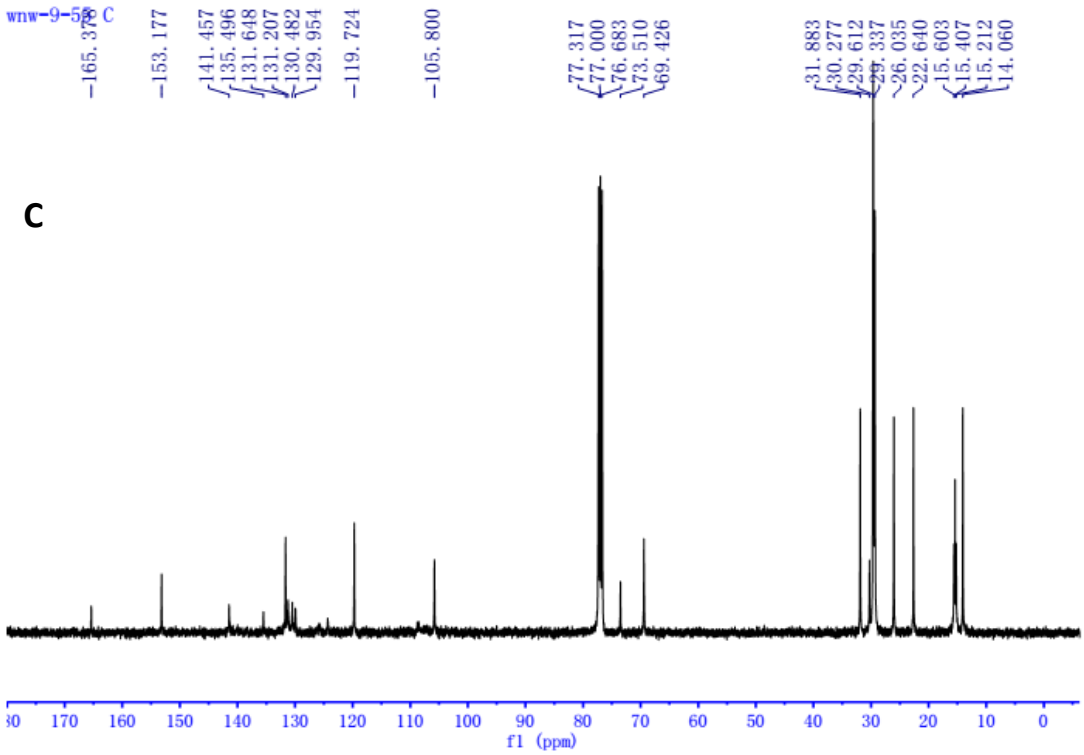

Fig. S8 The ^{1}H NMR (a), ^{31}P NMR (b), and ^{13}C NMR (c) spectra of **TPA** in $CDCl_3$.

11. The partial ^{31}P NMR spectra of 2 and TPA

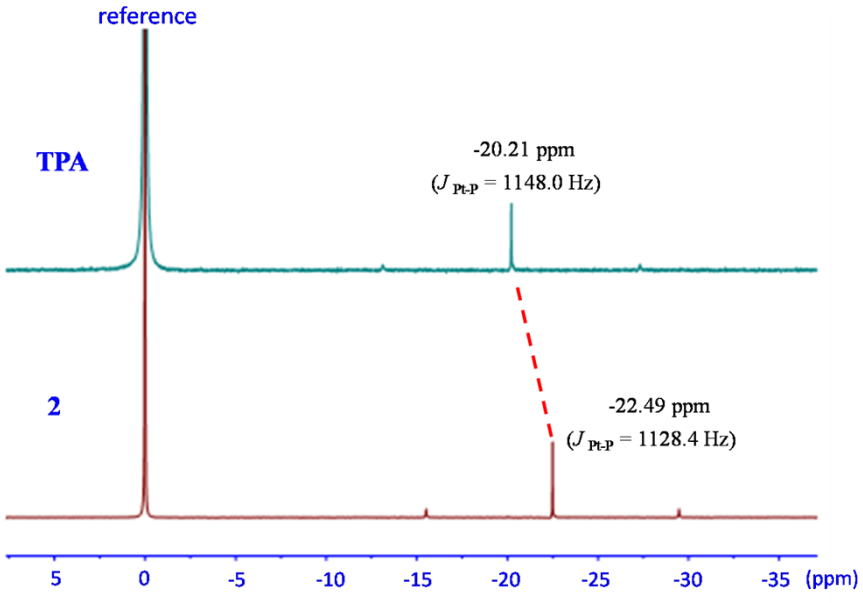

Fig. S9 The partial ^{31}P NMR spectra of **2** and **TPA** in $CDCl_3$.

12. MALDI-TOF-MS of TPA

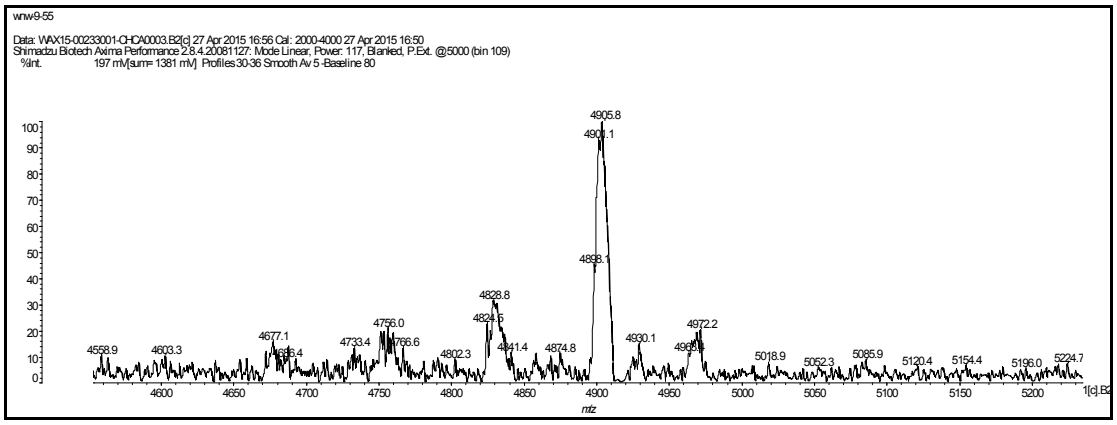

Fig. S10 MALDI-TOF-MS of **TPA.**

13. IR spectra of the xerogel TPA

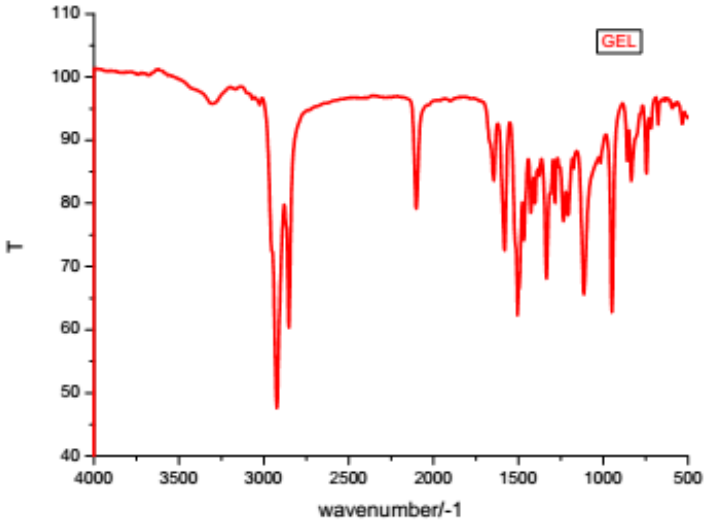

Fig. S11 IR spectra of the xerogel **TPA**.

14. X-ray diffraction diagrams of the xerogel TPA

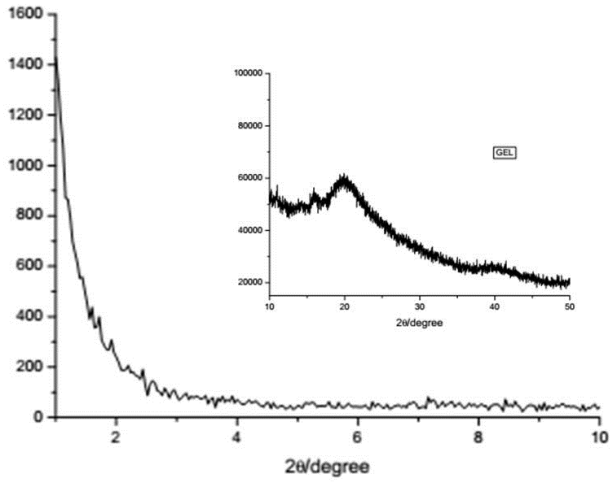

Fig. S12 X-ray diffraction diagrams of the xerogel **TPA**. The inset for the diffraction in wide-angle region.