Supporting Information

Self-assembled Nanostructures with Tridentate Cyclometalated Platinum(II) Complexes

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Experimental Section

Synthesis and Spectroscopic Characterization:

All starting materials were used as received from commercial sources. The ligand 6-(4'-methylphenyl)-2,2'-bipyridine (HC^N^N) was prepared according to literature methods. Elemental analyses were performed by the Institute of Chemistry at Chinese Academy of Sciences, Beijing. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix. Electrospray Ionization (ESI) mass spectra were obtained on a Finnigan LCQ quadrupole ion trap mass spectrometer (samples were dissolved in HPLC CH_3CN). ^1H, ^{13}C, ^{31}P, ^{19}F

and ^{195}Pt NMR spectra were recorded on Avance400 and 500 Bruker FT-NMR spectrometers with chemical shifts (in ppm) relative to tetramethylsilane (for ^{1}H and ^{13}C NMR) and external H_3PO_4 (for ^{31}P NMR) respectively. Infrared spectra were recorded on a Bio-Rad FT-IR spectrometer. UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer.

[(C^N^N)PtCl] (**2**). A mixture of 6-(4'-methylphenyl)-2,2'-bipyridine (HC^N^N) (192 mg, 0.78 mmol) and K_2PtCl_4 (300 mg, 0.72 mmol) in CH_3CN/H_2O (1:1 v/v, 50 mL) was refluxed for 18 hours. The resulted dark red solution was evaporated to dryness under reduced pressure. The residue was extract with CH_2Cl_2 (100 mL × 3) and the extracts was evaporated to dryness. Pure product (250 mg, yield 73%) was isolated as an orange solid by slow diffusion of Et_2O vapor into a concentrated DMF solution. Anal. Calcd for $C_{17}H_{13}ClN_2Pt$: C, 42.94; H, 2.76; N, 5.90. Found: C, 43.10; H, 2.47; N, 6.27. MS (+ve FAB): *m/z* 475 [M^+], 440 [M^+ – Cl]. ^{1}H NMR (d_6-DMSO): δ 8.86 (d, 1H, J = 5.0 Hz), 8.45 (d, 1H, J = 7.9 Hz), 8.31 (t, 1H, J = 7.7 Hz), 8.13–8.10 (m, 2H), 7.88 (t, 1H, J = 6.0 Hz), 7.86 (t, 1H, J = 7.4 Hz), 7.45 (d, 1H, J = 7.7 Hz), 7.28 (s with ^{195}Pt satellites, 1H, J_{PtH} = 43.6 Hz), 6.87 (d, 1H, J = 7.7 Hz), 2.28 (s, 3H).

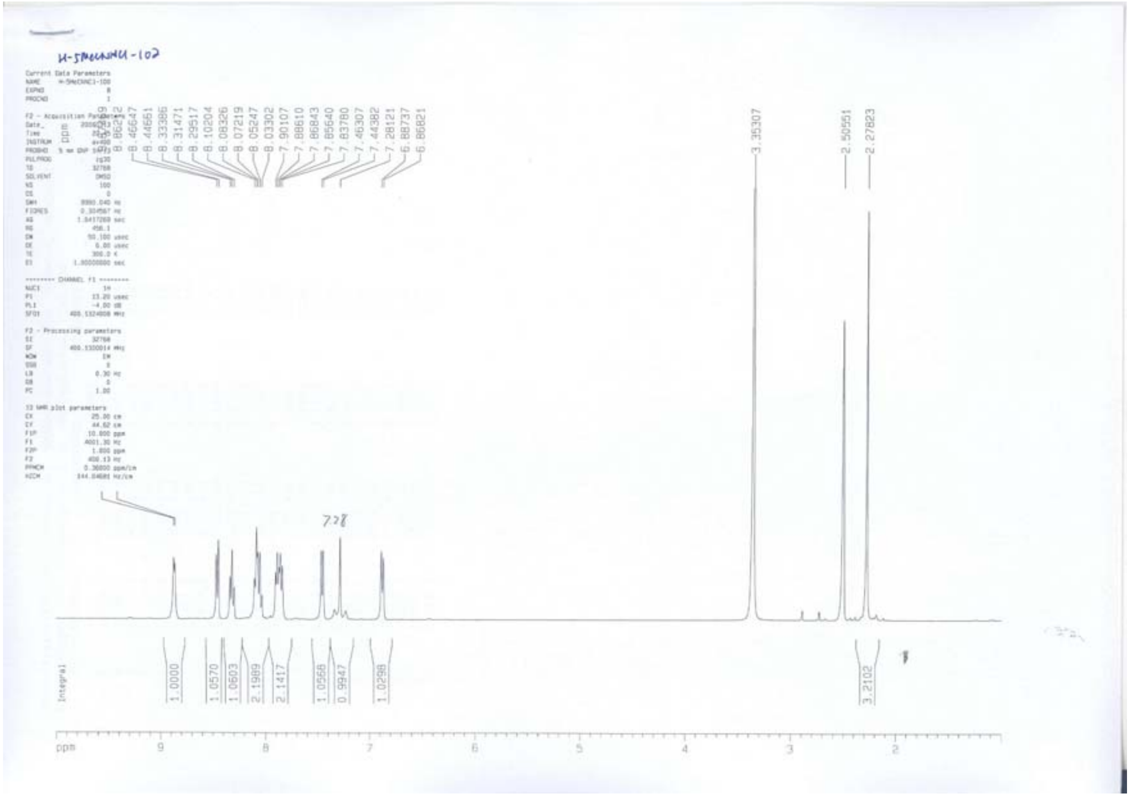


Figure S1. ^{1}H NMR spectrum of **2** in d_6-DMSO.

[(C^N^N)PtC≡O](PF$_6$) (**3**). A mixture of **2** (100 mg, 0.21 mmol) and AgOTf (60 mg, 0.23 mmol) in CH$_3$CN (30 mL) was refluxed for 2 hours. The resulted suspension was filtered through celite when it was still hot. Orange micro-needles precipitated out when the filtrate was cooled down. This precipitate was proved to be [(C^N^N)PtN≡CCH$_3$](OTf). X-ray crystallographic study on a single crystal of [(C^N^N)PtN≡CCH$_3$](PF$_6$) has revealed that the [(C^N^N)PtN≡CCH$_3$]$^+$ moieties are linked by Pt···Pt interactions into a dimeric structure in the solid state. The details will be reported elsewhere. To the hot (50 ^{o}C) solution of [(C^N^N)PtN≡CCH$_3$](OTf) in CH$_3$CN was bubbled carbon monoxide (CO) gas for 10 minutes and the resulted yellow solution was stirred overnight at room temperature under a CO atmosphere. The solvent was evaporated to dryness and the resulted orange solid was dissolved with 20 mL CH_3OH. The CH_3OH solution was filtered into a saturated NH_4PF_6 solution in CH_3OH. The resulted orange-brown solid was collected on sinter-glass filter and washed with copious of water, CH_3OH and Et_2O. Recrystallization by slow diffusion of Et_2O into a concentrated CH_3CN solution yieled orange-brown solid (85 mg, 66%). Anal. Calcd for $C_{18}H_{13}N_2OPtPF_6$: C, 35.23; H, 2.14; N, 4.57. Found: C, 35.71; H, 2.45; N, 4.15. MS (+ve FAB): *m*/*z* 468 [M^+]. IR (KBr): ν = 2109 (C≡O) cm^{-1}. ^1H NMR (d_6-DMSO): δ 8.99 (d, 1H, *J* = 4.9 Hz), 8.47–8.43 (m, 2H), 8.20 (t, 1H, *J* = 7.9 Hz), 8.15 (d, 1H, *J* = 7.7 Hz), 7.97 (t, 1H, *J* = 8.0 Hz), 7.88 (t, 1H, *J* = 6.0 Hz), 7.51 (d, 1H, *J* = 7.8 Hz), 6.94 (d, 1H, *J* = 7.8 Hz), 6.81 (s with ^{195}Pt satellites, 1H, J_{PtH} = 44 Hz), 2.08 (s, 3H).

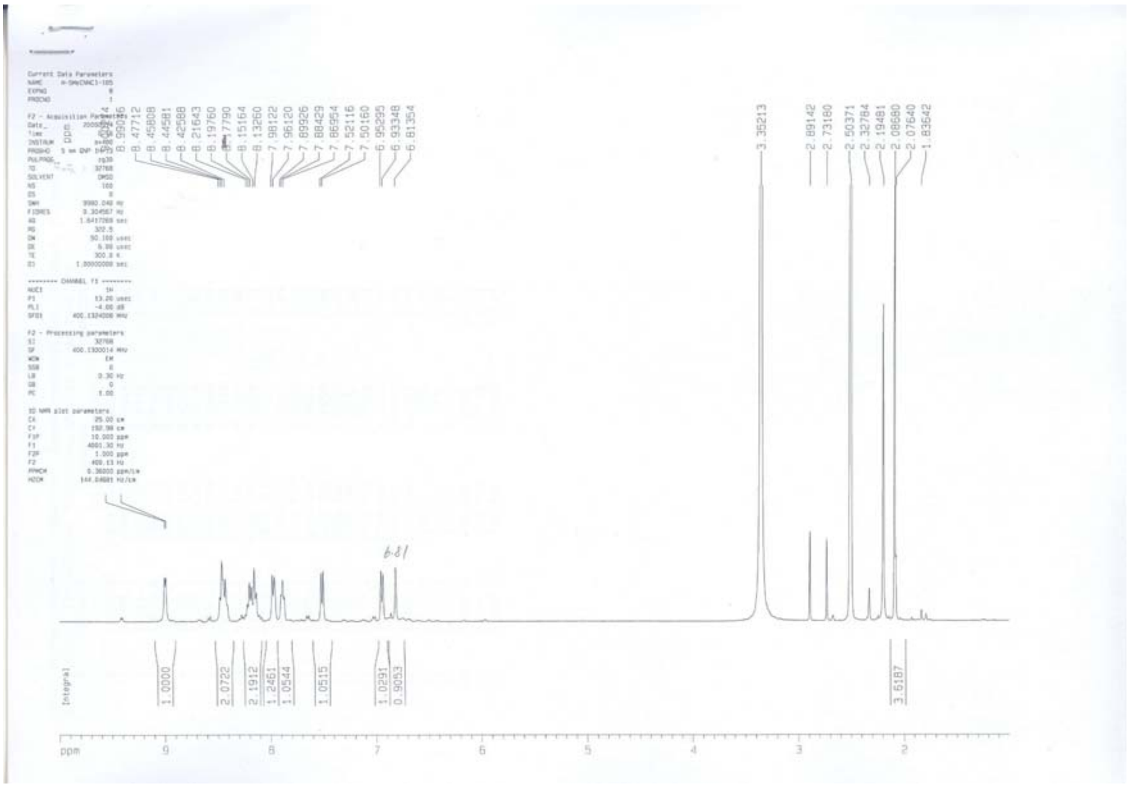


Figure S2. ^1H NMR spectrum of **3** in d_6-DMSO.

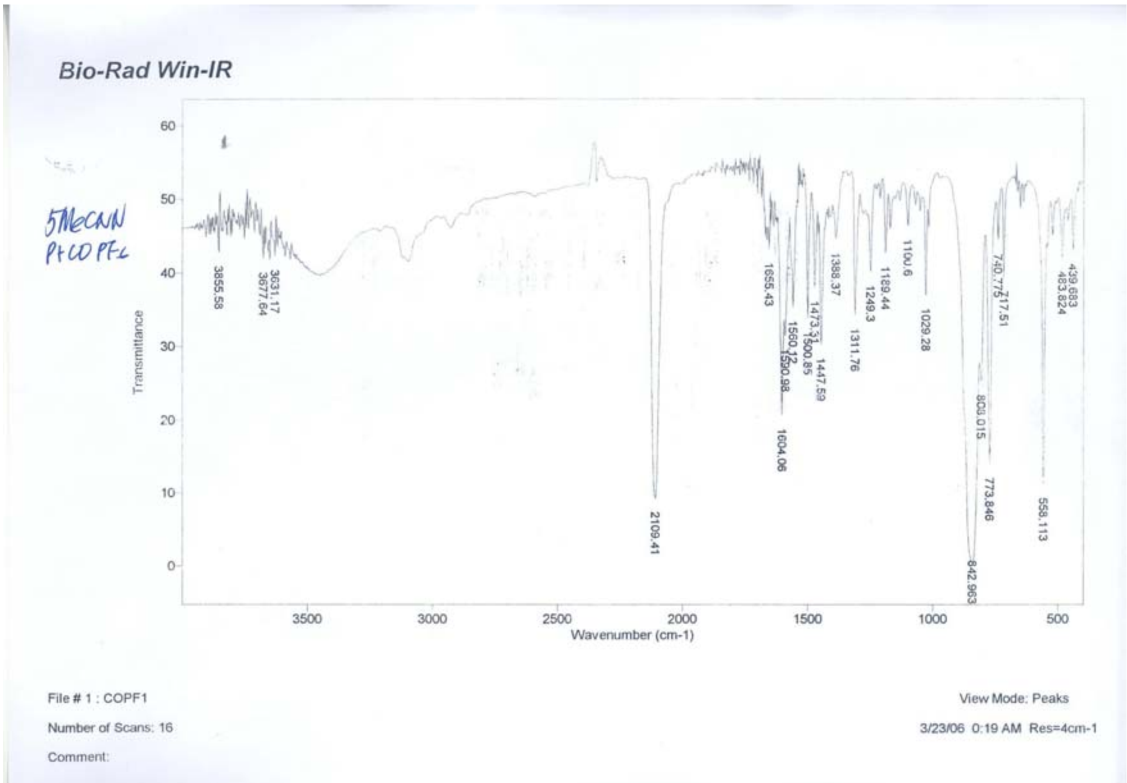


Figure S3. IR absorption spectrum of **3** in KBr pellet.

{[(C^N^N)PtCl][(C^N^N)PtC≡O]}(PF$_6$) (**1**). Two methods were applied to prepare this complex.

Method I (serendipity approach): To a solution of **2** (120 mg, 0.25 mmol) in CH_2Cl_2 (120 mL) was bubbled CO gas for 20 minutes. The resulted dark green solid was collected on a sinter-glass filter and washed thoroughly with CH_2Cl_2 and Et_2O. The solid (75 mg) was dissolved with DMF (1.5 mL) in the presence of NH_4PF_6 (20 mg). The resulted dark red solution was filtered into water (30 mL) to give a dark blue precipitate which was collected on a sinter-glass filter and washed thoroughly with water, CH_3OH, CH_2Cl_2 and Et_2O. Yield: 48% based on **2**.

Method II (rational approach): The mixture of **2** (19.0 mg, 0.04 mmol) and **3** (24.5 mg, 0.04 mmol) in CH_3CN (5 mL) was stirred for 10 minutes. The resulted red solution was filtered and evaporated to dryness to give a dark blue solid which was collected on a sinter-glass filter and washed thoroughly with CH_3OH, CH_2Cl_2 and Et_2O. Yield: >80%.

Anal. Calcd for $C_{35}H_{26}N_4ClOPt_2PF_6$: C, 38.60; H, 2.41; N, 5.15. Found: C, 37.71; H, 2.04; N, 4.65. MS (ESI): *m/z* 942.5 [M^+], 468.1 {M^+ – [(C^N^N)PtCl]}. IR (KBr): ν = 2094 (C≡O) cm^{-1}. ^1H NMR (d_6-DMSO): δ 8.87 (d, 1H, *J* = 5.0 Hz), 8.80 (d, 1H, *J* = 4.9 Hz), 8.31 (d, 1H, *J* = 7.7 Hz), 8.25 (d, 1H, *J* = 7.5 Hz), 8.14 (virtual d, 2H), 8.02 (t, 1H, *J* = 8.0 Hz), 7.97–7.80 (m, 4H), 7.76 (d, 1H, *J* = 7.8 Hz), 7.68 (d, 1H, *J* = 8.2 Hz), 7.54 (d, 1H, *J* = 7.9 Hz), 7.23 (d, 1H, *J* = 7.8 Hz), 7.14 (d, 1H, *J* = 7.8 Hz), 6.85 (d, 1H, *J* = 7.9 Hz), 6.74 (d, 1H, *J* = 5.6 Hz), 6.70 (s with ^{195}Pt satellites, 1H), 6.30 (s with ^{195}Pt satellites, 1H), 2.09 (s, 3H), 2.06 (s, 3H). ^1H NMR (CD_3CN): δ 8.66 (d, 1H, *J* = 4.2 Hz), 8.55 (d, 1H, *J* = 4.4 Hz), 7.97 (t, 1H, *J* = 7.8 Hz), 7.92 (t, 1H, *J* = 7.8 Hz), 7.61 (t, 1H, *J* = 8.0 Hz), 7.56 (t, 1H, *J* = 5.4 Hz), 7.52 (t, 1H, *J* = 5.5 Hz), 7.49 (t, 1H, *J* = 7.9 Hz), 7.41 (d, 1H, *J* = 8.5 Hz), 7.39 (d, 1H, *J* = 8.1 Hz), 7.11 (d, 1H, *J* = 7.8 Hz), 7.00 (t, 1H, *J* = 7.3 Hz), 6.91 (d, 1H, *J* = 7.9 Hz), 6.68–6.62 (m, 3H), 6.55 (d, 1H, *J* = 7.9 Hz), 6.28 (s with ^{195}Pt satellites, 1H), 5.85 (s with ^{195}Pt satellites, 1H), 2.09 (s, 3H), 1.88 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 207.8 (*C*≡O), 169.6, 165.7, 164.4, 157.7, 156.9, 155.7, 155.2, 154.9, 148.8, 144.4, 144.3, 143.9, 143.7, 143.1, 141.7, 141.5, 140.5, 139.5, 138.5, 137.4, 134.7, 129.1, 128.7, 127.9, 127.0, 125.6, 125.0, 124.1, 120.9, 120.5, 119.8, 119.6, 22.2 (Me), 21.8 (Me). $^{195}Pt\{^1H\}$ NMR (CD_3CN): δ –3832.7 (virtual s). $^{19}F\{^1H\}$ NMR (CD_3CN): δ –72.5 (d, J_{PF} = 708 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN): δ –144.5 (virtual quintet, J_{PF} = 706 Hz).

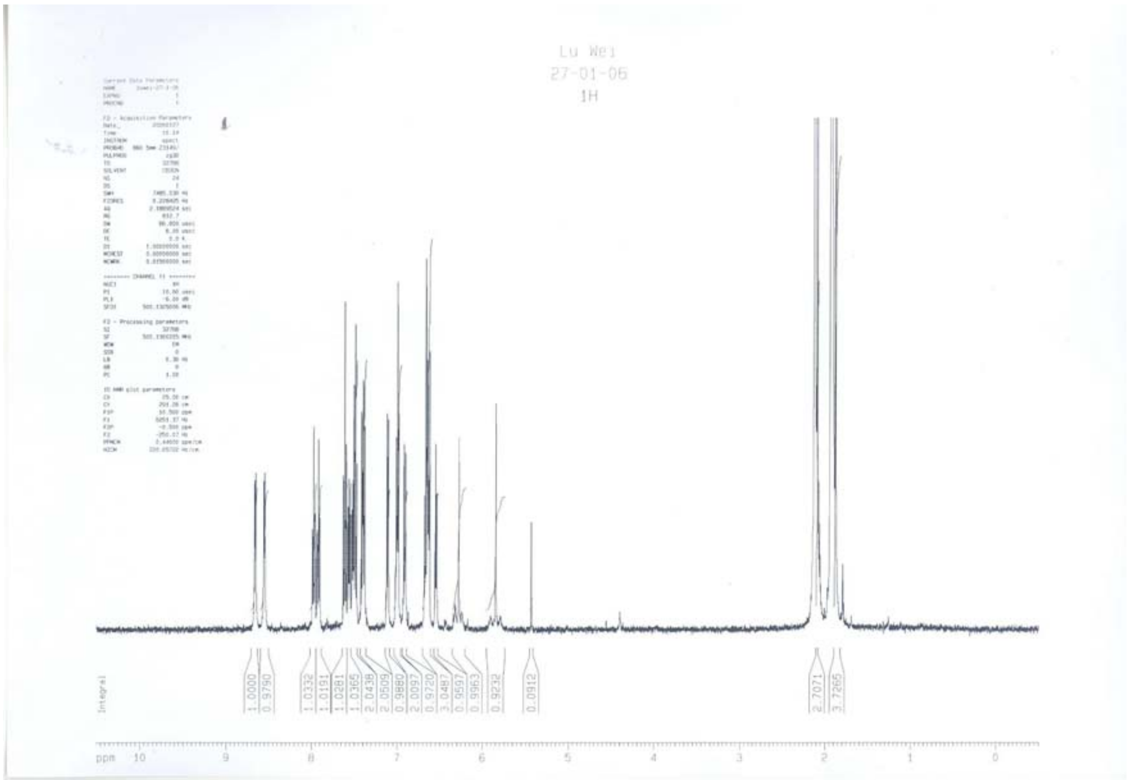


Figure S4. ^{1}H NMR spectrum of **1** in CD_3CN.

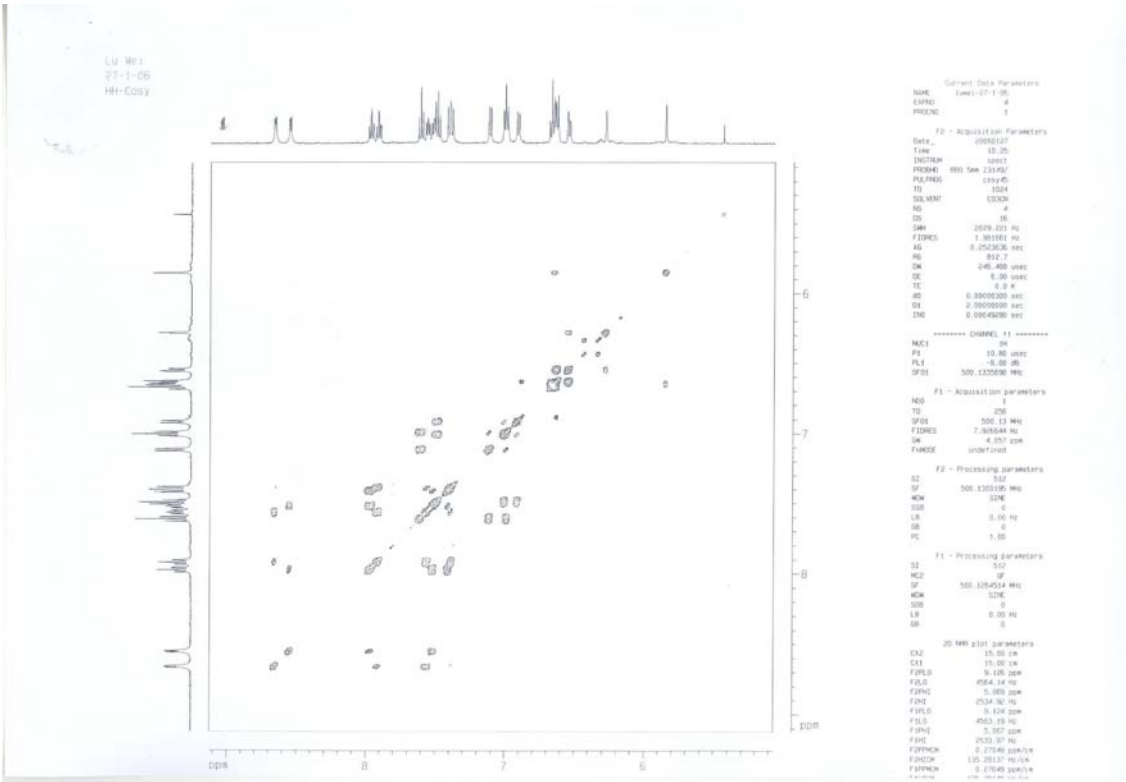


Figure S5. 2D H-H COSY NMR spectrum of **1** in CD_3CN.

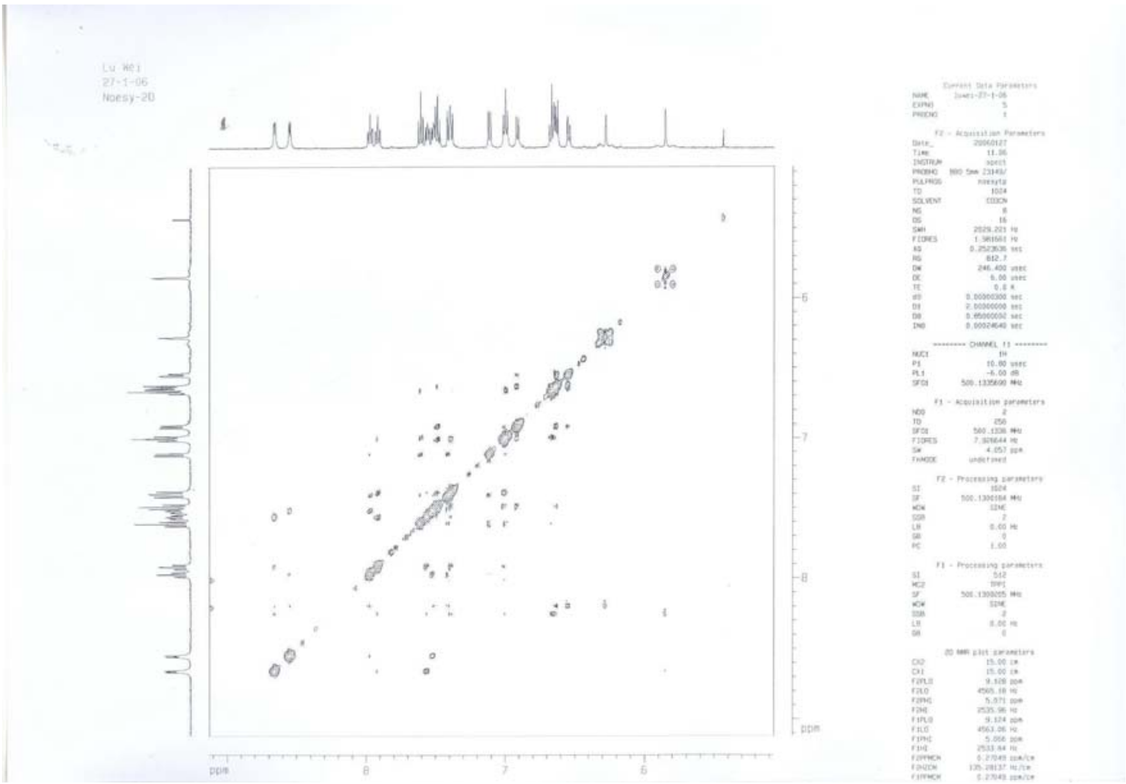


Figure S6. 2D NOESY NMR spectrum of **1** in CD_3CN.

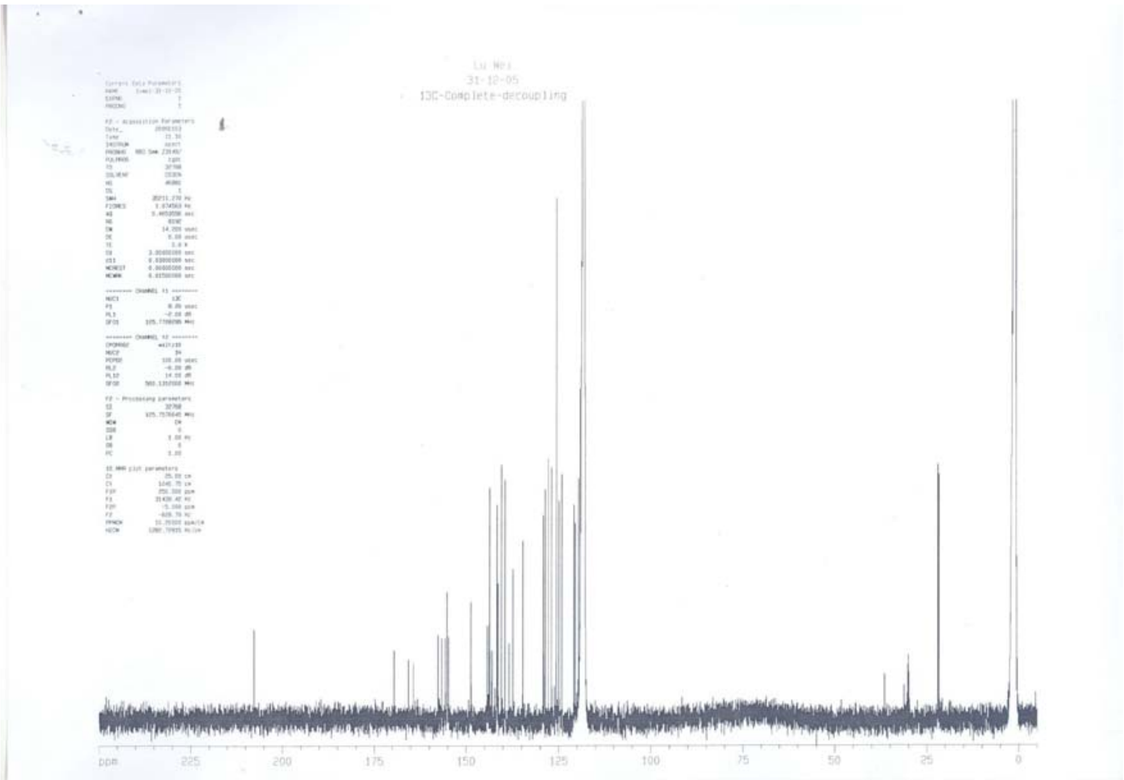


Figure S7. ^{13}C NMR spectrum of **1** in CD_3CN.

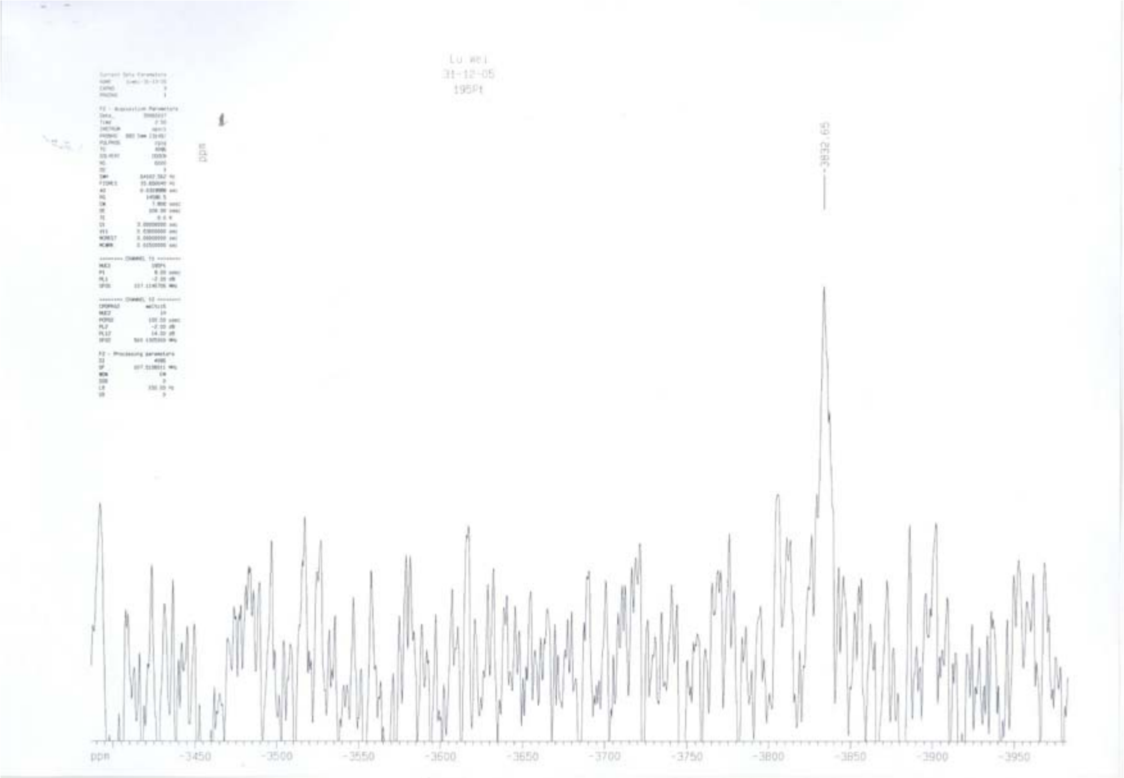


Figure S8. ^{195}Pt NMR spectrum of **1** in CD_3CN.

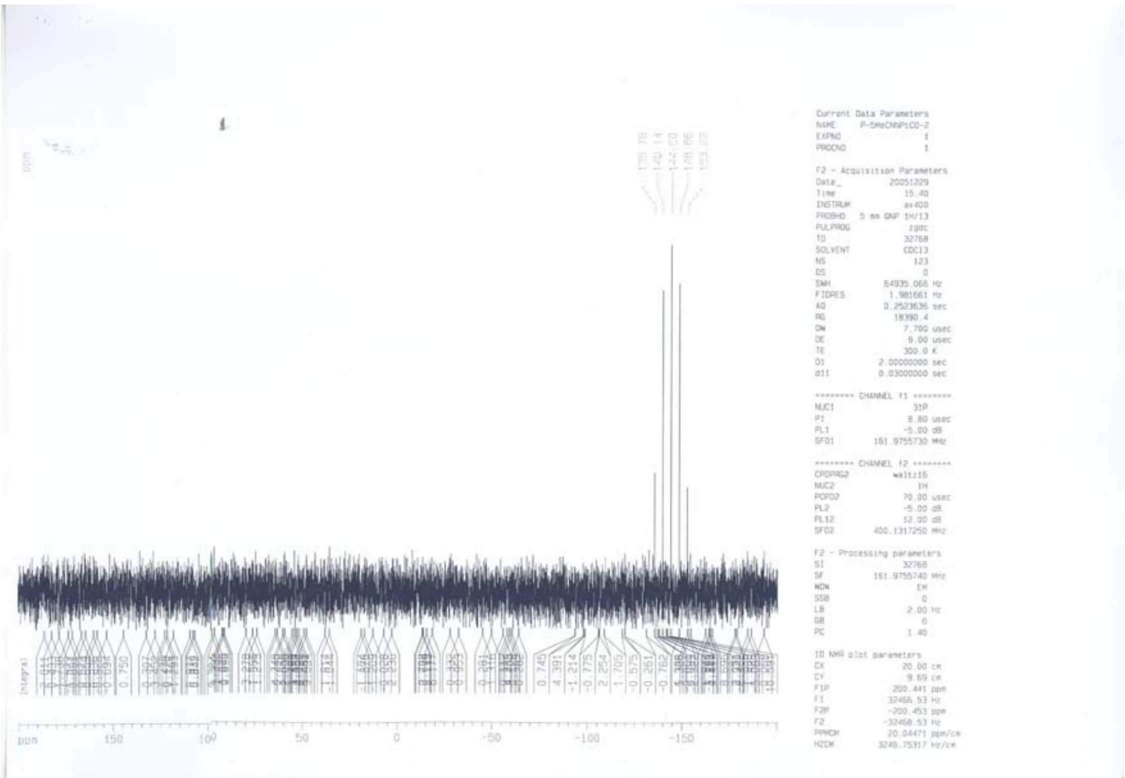


Figure S9. ^{31}P NMR spectrum of **1** in CD_3CN.

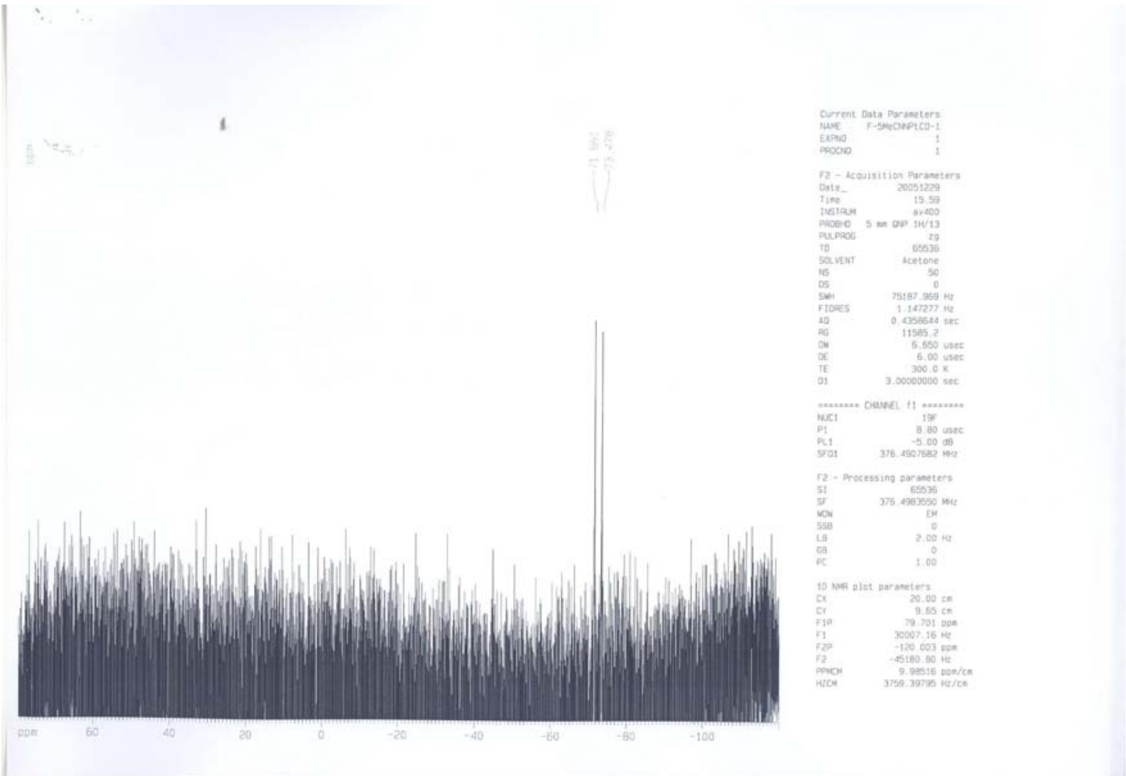


Figure S10. ^{19}F NMR spectrum of **1** in CD_3CN.

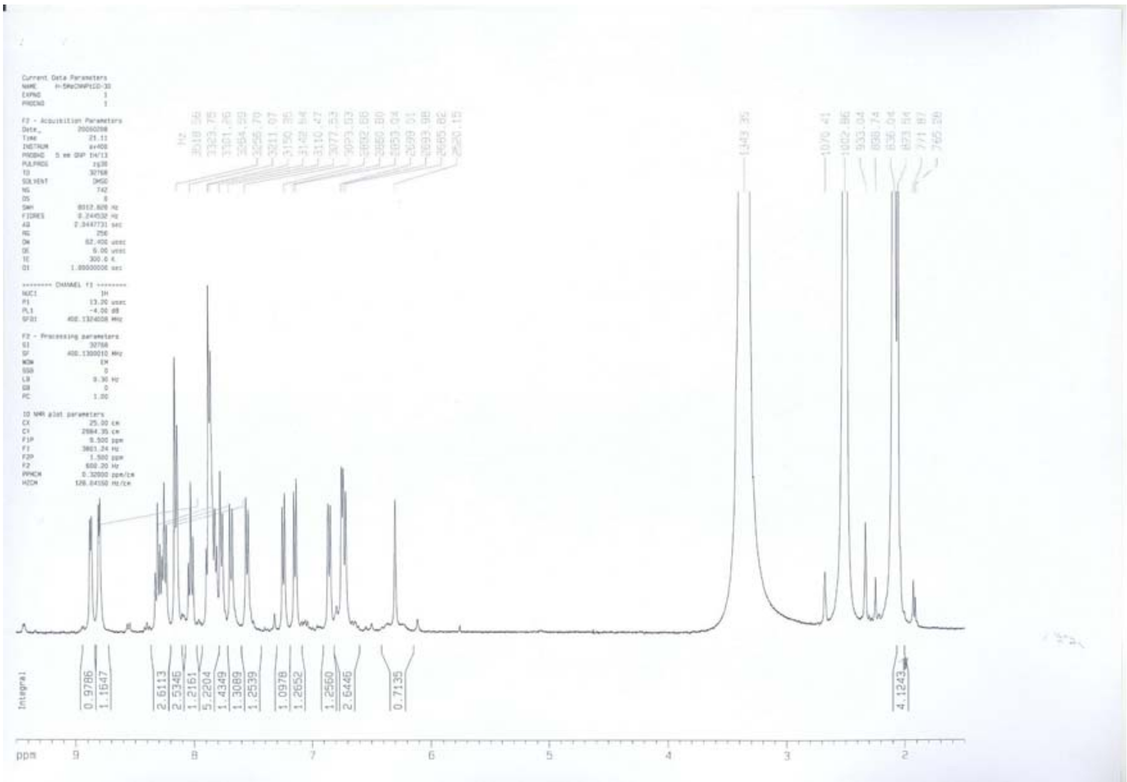


Figure S11. ^{1}H NMR spectrum of **1** in d_6-DMSO.

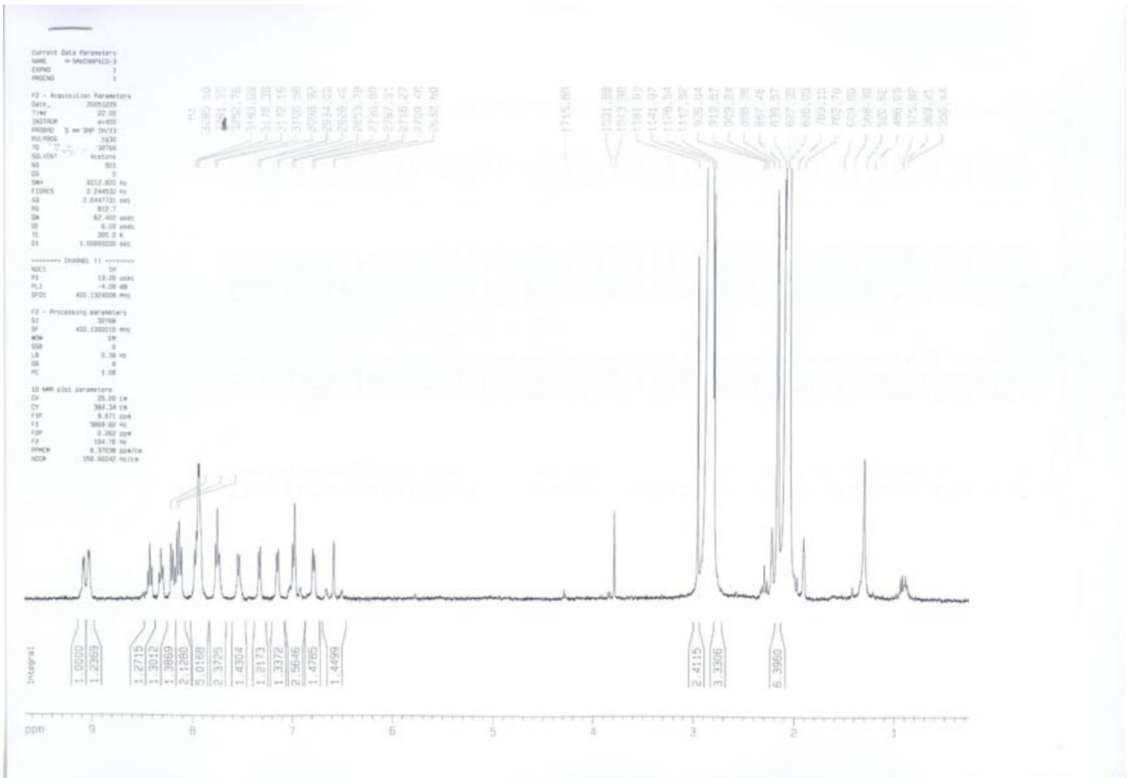


Figure S12. ^{1}H NMR spectrum of **1** in d_6-acetone (nanowire dispersion with concentration being ~2×10^{-3} M).

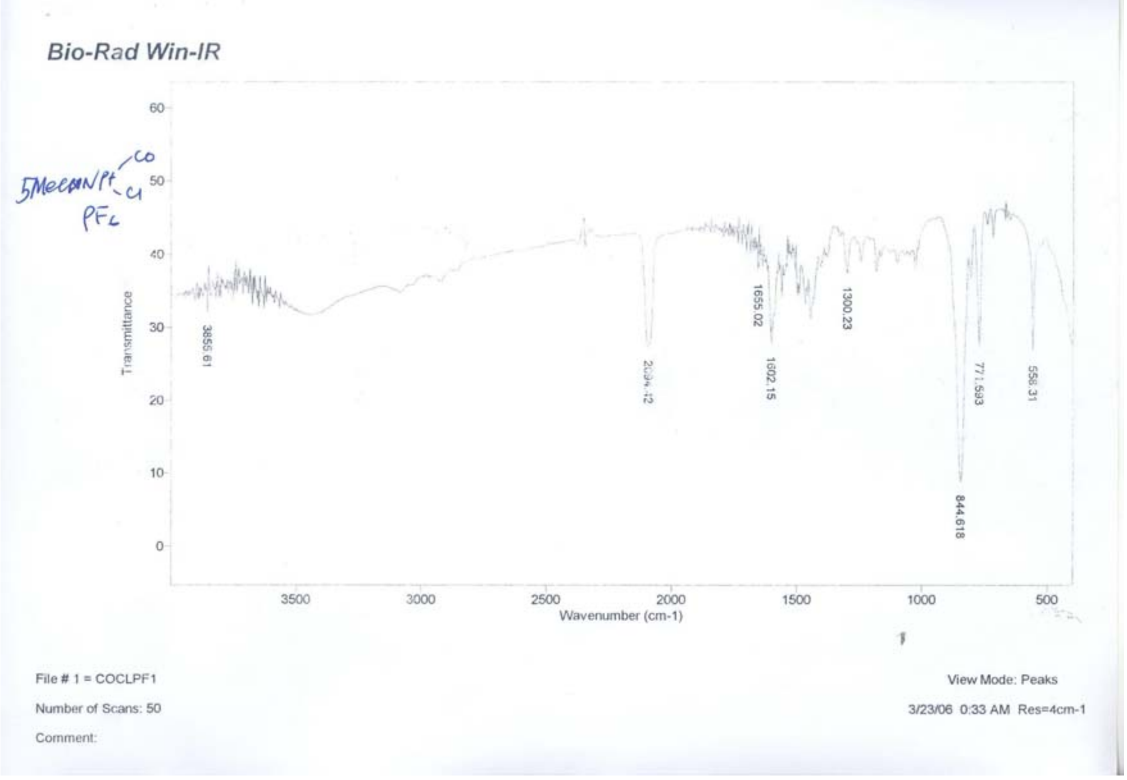


Figure S13. IR absorption spectrum of **1** in KBr pellet.

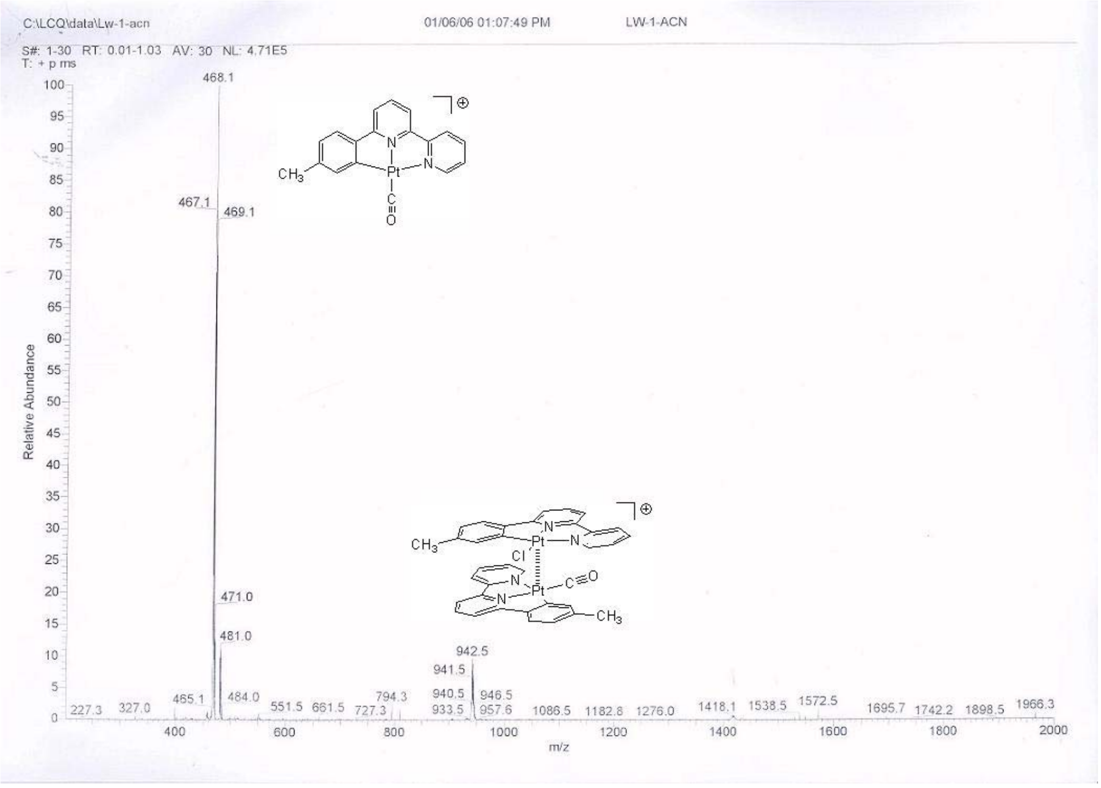


Figure S14. ESI-MS spectrum of **1** in CD_3CN.

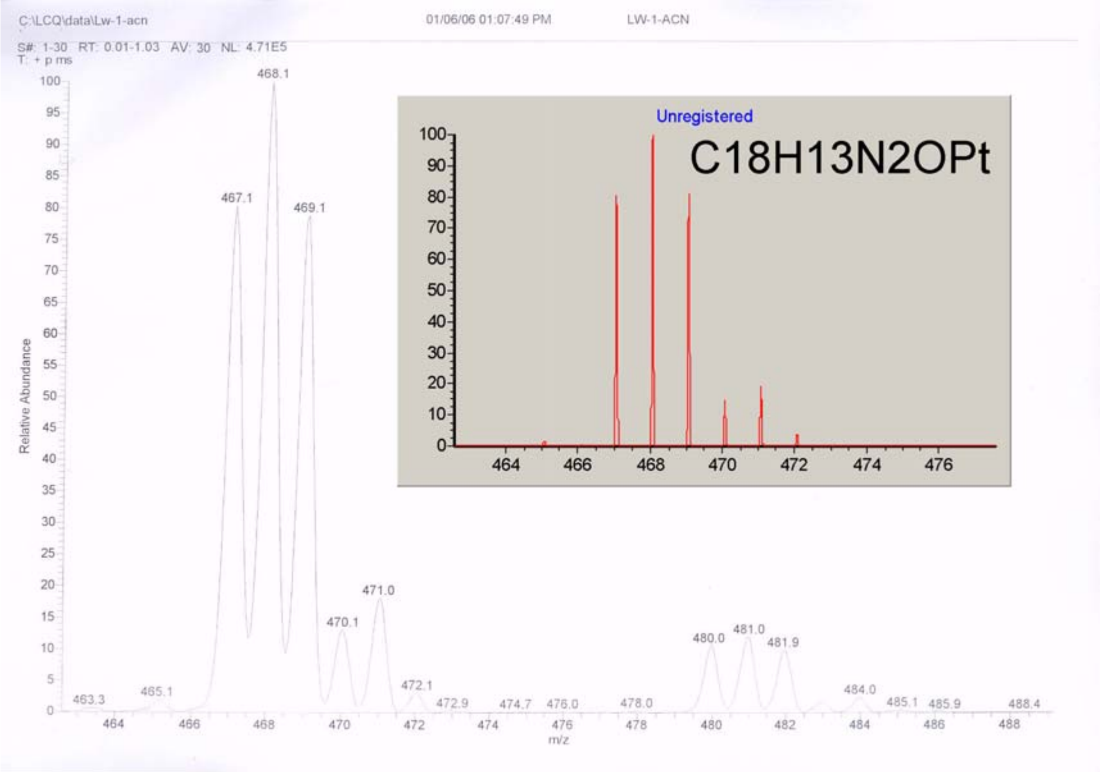


Figure S15. Experimental and stimulated (inset) isotopic pattern of $[(C\text{^}N\text{^}N)PtC{\equiv}O]^+$ ($C_{18}H_{13}N_2OPt$).

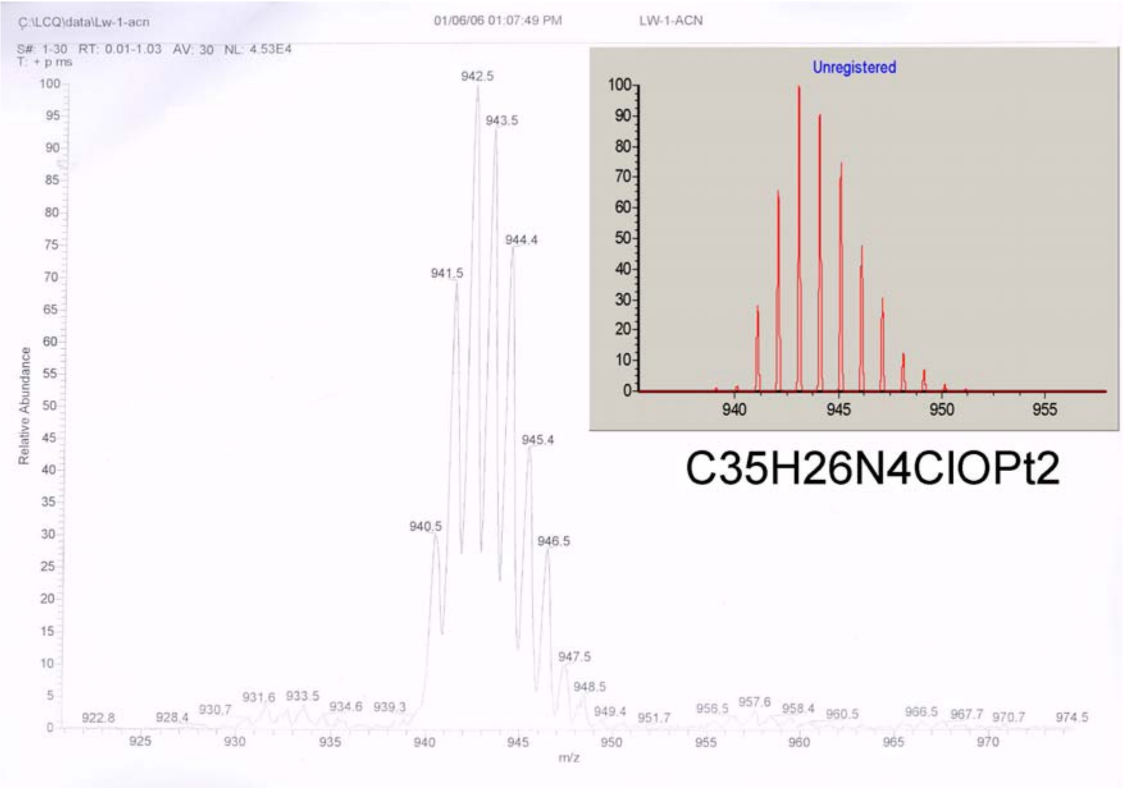


Figure S16. Experimental and stimulated (inset) isotopic pattern of {[(C^N^N)PtCl][(C^N^N)PtC≡O]}$^+$ ($C_{35}H_{26}N_4ClOPt_2$).

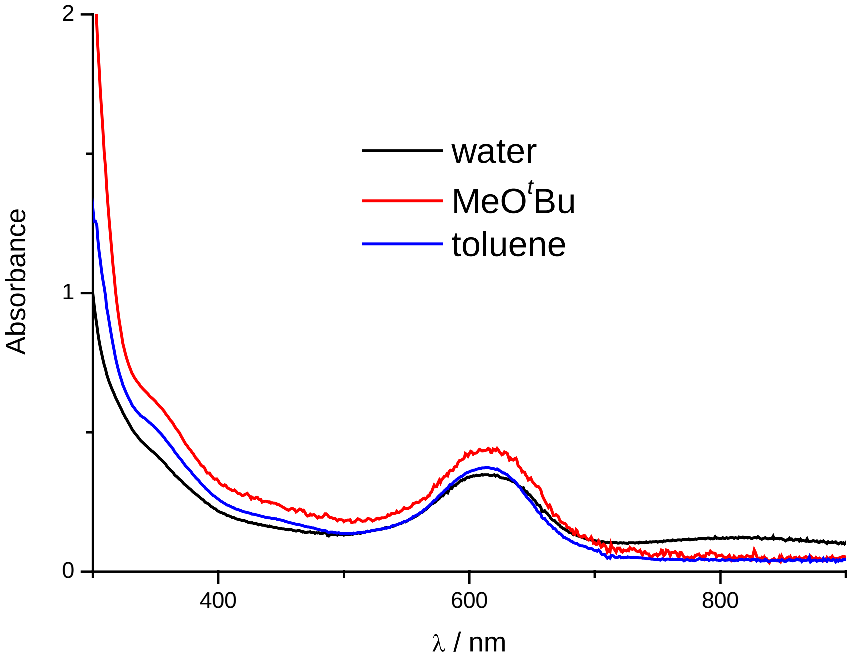


Figure S17. UV-vis absorption spectra of **1** dispersed in various poor solvents (prepared by injecting 100 μL 1.2 × 10^{-3} M acetone solution into 10 mL poor solvent).

TEM, SEM and FET Devices:

TEM images and SAED pictures were recorded on a Philips Tecnai 20 electron microscope (accelerating voltage of 200 kV). The SEM images were taken on a LEO 1530 scanning electron microscope operating at 5.0 kV. A few drops of the nanowire dispersion were deposited on the copper grid and the excess solvent was removed by a piece of filter paper. All the samples for SEM observations were sputtered with gold thin film (20 second, <2 nm thickness).

The XRD pattern of the nanostructured thin film was recorded on a Philips PW1830 powder X-ray diffractometer operating with graphite monochromatized Cu Kα radiation (λ = 1.540562 Å) and nickel filter. The scanning rate is 0.5° min^{-1} in the 2θ range from 2 to 70°.

A common substrate-gate structure field effect transistor (FET) was fabricated. The SiO_2 layer (100 nm, relative permittivity = 3.9), heavily doped n-type Si substrates, Ti adhesion film (10 nm, lower)/Au conductive film (50 nm, upper) were used as the insulator, gate electrode and source/drain electrodes, respectively. The transistor output and transfer characteristics were measured with a probe station under nitrogen atmosphere using a Keithley K4200 semiconductor parameter analyzer. The transistor channel length and widths were 5 and 1035 μm respectively.

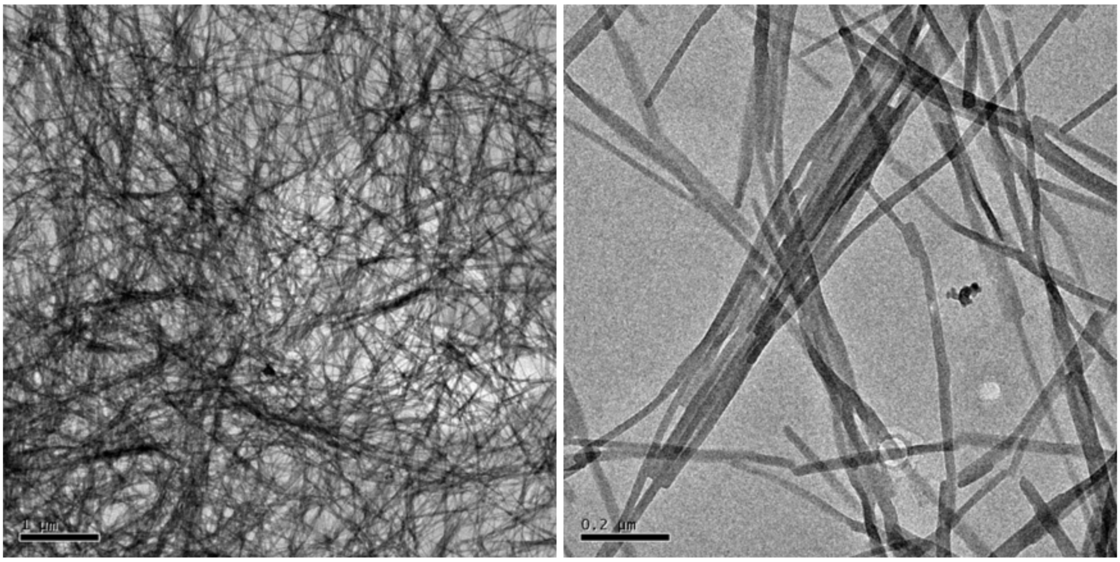


Figure S18. TEM image of **1** dispersed in acetone (concentration ~6 × 10^{-3} M).

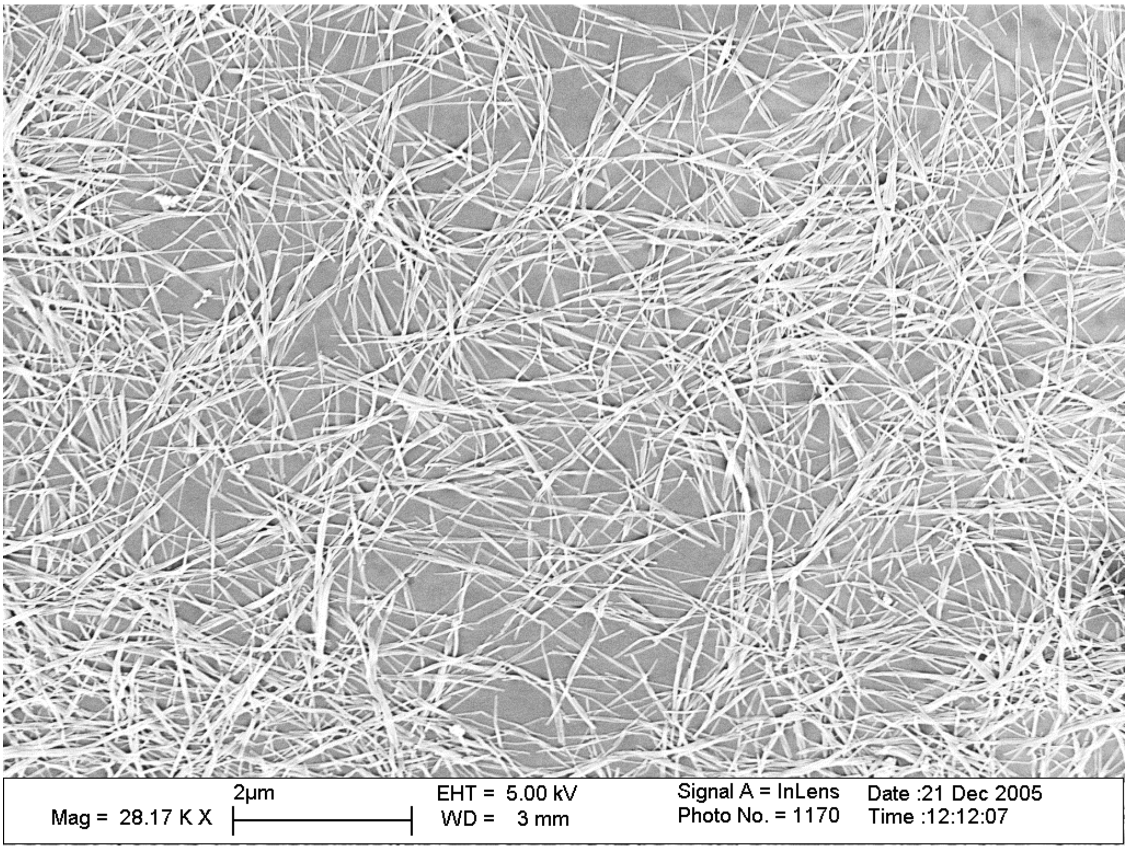
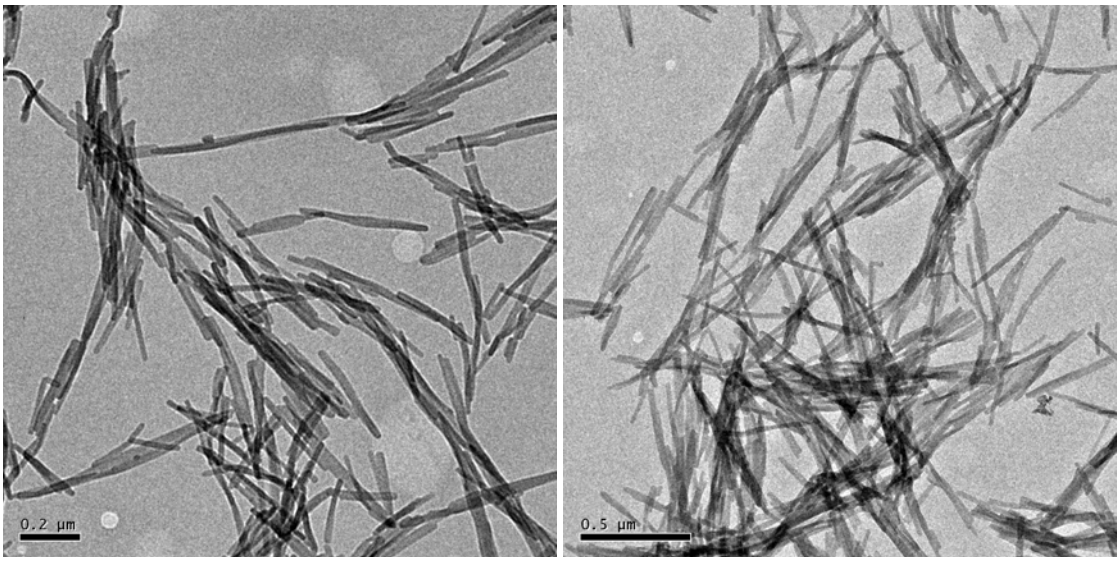
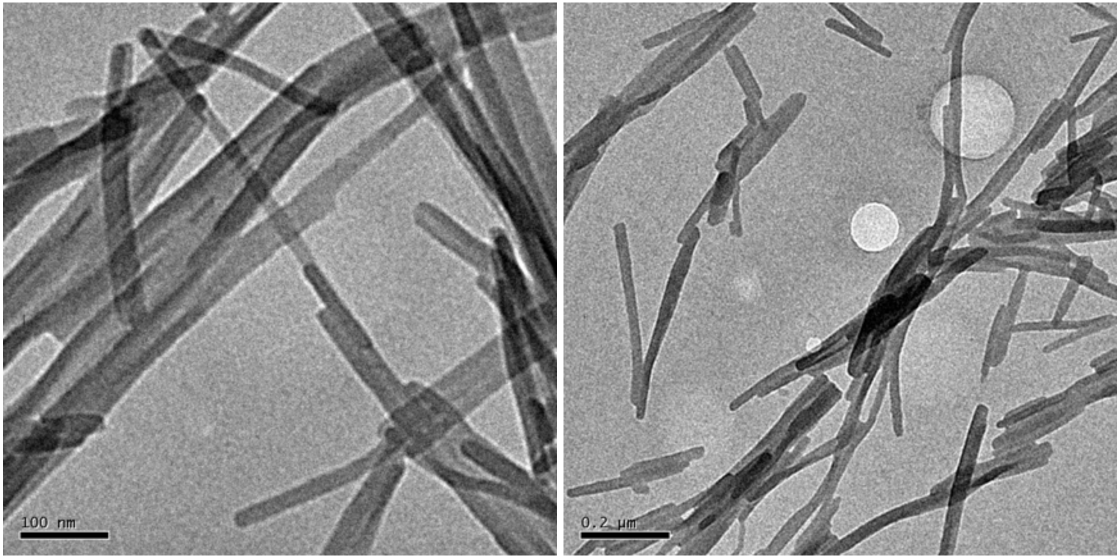


Figure S19. SEM image of **1** dispersed in acetone (concentration ~6 × 10^{-3} M).



in cyclohexane in Et_2O



in toluene in water

Figure S20. TEM image of **1** dispersed in various poor solvents.

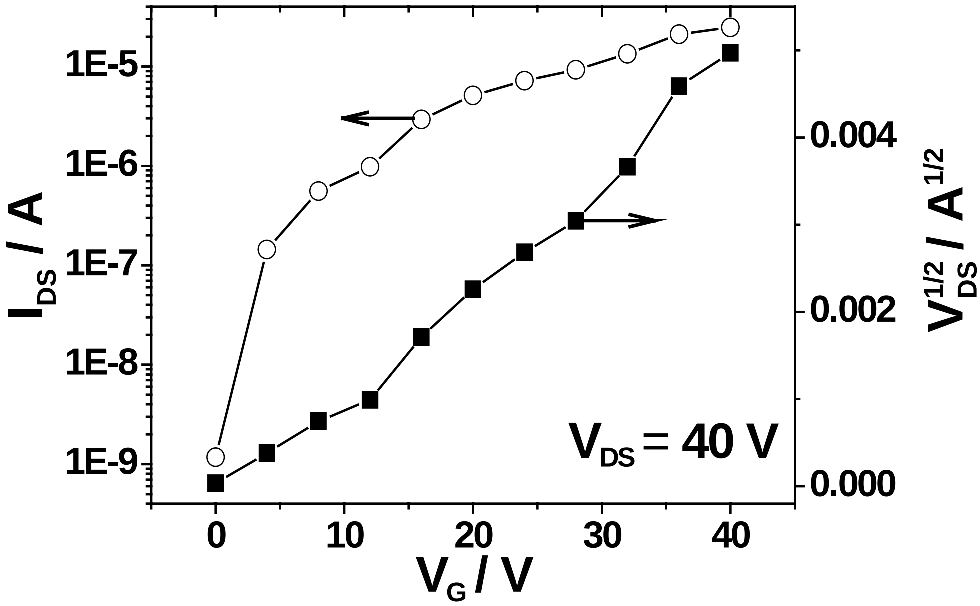


Figure S21. Transfer (I_{DS} vs. V_G) characteristics of the TFT device with nanostructured **1** as semiconducting layer.

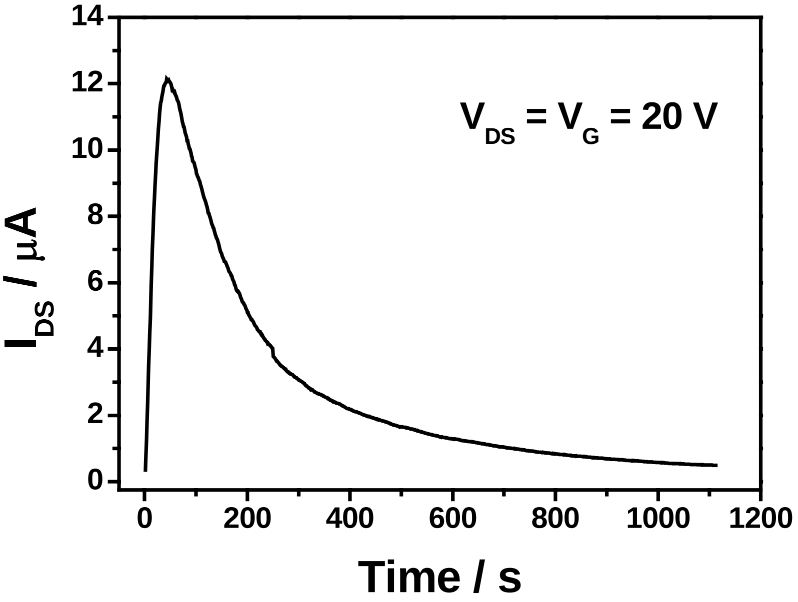


Figure S22. Transient measurement (V_{DS} = V_G = 20 V) of the TFT device with nanostructured **1** as semiconducting layer.