

Electronic Supplementary Information

Dipyrrin complex assisted in-situ synthesis of ultra-small gold nanoparticles decorated on partially reduced graphene oxide nanocomposite for efficient catalytic reduction of Cr(VI) to Cr(III)

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EXPERIMENTAL SECTION

Reagents. All the reactions have been performed in deaerated solvents under nitrogen atmosphere. The solvents were purified following literature procedure prior to its use.¹⁵ Diethyl amine, carbon disulfide, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 4-fluorobenzaldehyde, H₂AuCl₄, pyrrole, and nickel(II) chloride hydrate were procured from Sigma Aldrich Chemical Co., USA and used as received without further purifications. The precursor complex [Ni(dedtc)₂] and pypdmH [1-(pyridin-2-yl)piperazinephenyl-dipyrromethane] were synthesized and purified by literature procedures.¹⁶

General Methods. Elemental analyses for carbon, hydrogen, and nitrogen were performed on an Exeter Analytical Inc. model CE-440 CHN analyzer. IR and UV-vis spectra were acquired on a Varian 3300 FT-IR, Shimadzu UV-1601. ¹H (300 MHz) and ¹³C (75.45 MHz) NMR spectra were obtained on a JEOL AL300 FT-NMR spectrometer using tetramethylsilane [Si(CH₃)₄] as an internal reference. Electrospray ionization mass spectrometric (ESI-MS) measurements were made on a THERMO Finnigan LCQ Advantage Max ion trap mass spectrometer. In a typical measurement, samples (10 μL) were dissolved in dichloromethane/acetonitrile (3:7, v/v) and introduced into the ESI source through a Finnigan surveyor auto sampler. Mobile phase (MeOH/MeCN:H₂O, 90:10) flowed at a rate of 250 μL/min. Ion spray and capillary voltage were set at 5.3 KV and 34 V, respectively. The MS scans were run upto 2.5 min and spectra print-outs averaged of over 10 scans. TEM and HRTEM images were captured on HR TEM (JEOL JEM 2100) and FEI Technai 20 U Twin Transmission Electron Microscope. The samples were loaded over lacy carbon coated copper TEM grids (300 mesh) dried under ambient conditions, and imaged. Elemental mapping on the samples were performed using *in-situ* EDX-STEM (Oxford Instrument Inc, INCA X-sight).

Synthesis:

Synthesis of ligand 1-(pyridine-2-yl)piperazinephenyldipyrromethane (pypdpmH)

To a degassed solution of 4-(4-pyridin-2-yl)piperazin-1-yl)benzaldehyde (2.68 g, 10.0 mmol) and pyrrole (6.9 mL, 100.0 mmol), catalytic amounts of trifluoroacetic acid (15.4 μL, 0.20 mmol) were added and stirred for 1 h under nitrogen atmosphere and then heated at 70 °C overnight. The reaction mixture was dissolved in CH₂Cl₂ (50 mL) washed with 0.1 M NaOH (50 mL) followed by water (50 mL), dried over Na₂SO₄ and concentrated under

reduced pressure. Flash chromatography of the crude product over silica gel (SiO₂; hexanes:CH₂Cl₂, 1:1) yielded the dipyrromethane (pypdpmH) as a white solid. Yield: 75% (2.87 g). Anal. Calc for C₂₄H₂₅N₅: requires: C, 75.17; H, 6.57; N, 18.26. Found: C, 62.21; H, 5.12; N, 6.91%. ¹H NMR (CDCl₃, δ ppm): 3.23 (t, 4H, CH₂, piperazine), 3.97 (t, 4H, CH₂, piperazine), 5.42 (s, 1H, CH dipyrin), 5.92 (s, 2H, pyrrole), 6.14 (d, 2H, *J* = 3.0 Hz, pyrrole), 6.51 (t, 1H, pyridyl) 6.68 (s, 2H, pyrrole), 6.92 (d, 4H, *J* = 7.7 Hz, phenyl), 7.13 (d, 2H, *J* = 7.7 Hz, phenyl), 7.92 (bs, 2H, NH, pyrrole), 8.33 (d, 1H, *J* = 3.9 Hz, pyridyl). ¹³C NMR (CDCl₃ δ ppm): 43.07 (piperazine), 45.25 (piperazine), 49.10 (*meso*-C), 106.94, 107.22, 108.28, 113.55, 116.33, 117.00, 129.09, 132.92, 133.47, 137.53, 147.95, 150.08, 159.37 (dipyrin). ESI-MS. (Calcd, found, *m/z*) 384.2110, 384.2110 [M + H]⁺.

Synthesis of [Ni(pypdpm)(dedtc)] (1)

DDQ (0.114 g, 0.50 mmol) dissolved in benzene (20 mL) was added drop wise with stirring to an ice cooled stirring solution of pypdpmH (0.191 g, 0.50 mmol, dichloromethane, 30 mL) and reaction mixture stirred for an additional 1 h at room temperature (rt). After filtration it was concentrated to dryness under reduced pressure to afford a red brown solid. Resulting mass thus obtained was dissolved in dichloromethane (40 mL) and filtered to remove any solid impurities. Triethylamine (1 mL) and precursor complex [Ni(dedtc)₂] (0.182 g, 0.50 mmol) were successively added to the filtrate and resulting reaction mixture stirred overnight at rt. It was concentrated to dryness under reduced pressure and ensuing product purified by column chromatography (SiO₂; CH₂Cl₂/hexane, 60:40) to afford a red solid. Yield: (0.210 g; 72%). Anal. Calcd for C₂₉H₃₂N₆NiS₂: C, 59.29; H, 5.49; N 14.31. Found: C, 59.53; H, 5.35; N, 14.22. ¹H NMR (CDCl₃, δ_H ppm): 1.28 (t, 6H, CH₂CH₃), 3.36 (t, 4H, CH₂, piperazine) 3.66 (q, 4H, CH₂CH₃), 4.01 (t, 4H, CH₂, piperazine), 6.25 (d, 2H, *J* = 3.0 Hz, pyrrole) 6.53 (t, 1H, pyridyl), 6.66 (d, 2H, *J* = 3.6 Hz, pyrrole), 6.97 (d, 4H, *J* = 8.7 Hz, phenyl), 7.37 (d, 2H, *J* = 8.4 Hz, pyrrole), 8.34 (d, 2H, *J* = 4.8 Hz, pyrrole). ¹³C NMR (CDCl₃, δ_C ppm): 12.40, 43.62, 44.29, 48.59, 110.19, 114.36, 117.19, 131.86, 131.95, 135.65, 146.68, 149.39, 157.77, 202.43. ESI-MS. Calcd, found: *m/z* 586.1483, 587.0561 [M + H]⁺. UV-vis (*c*, 1 × 10⁻⁵; THF:H₂O, 10:90; λ_{max} nm, ε M⁻¹ cm⁻¹): 517 (1.67 × 10⁴), 456 (4.01 × 10⁴), 280 (6.46 × 10⁴).

Synthesis of gold nanoparticles (AuNPs) using complex 1

Synthesis of AuNPs have been achieved by using **1** (*c*, 1.0×10^{-5} , THF : H₂O, 10:90, 5 mL) and HAuCl₄ (*c*, 1.0×10^{-3} , H₂O, 5 μ L) at room temperature. The colloidal solution containing AuNPs is stable for over six months as evidenced by UV–vis spectral studies.

Dispersion of as-synthesized gold nanoparticles (AuNPs) on graphene oxide (GO)

The as-synthesized AuNPs were mixed with exfoliated graphene oxide in varying ratios (100, 300 and 500 mg/mL) by simply mixing for 5 min. It led to aggregation which was purified by centrifugation. The flocculated nanocomposites were dispersed in DMF and triple distilled water (5%, v/v) and used for analysis by UV–vis absorption spectroscopy, scanning electron (SEM) and transmission electron microscopy (TEM) analyses.

X-ray Structure Determination

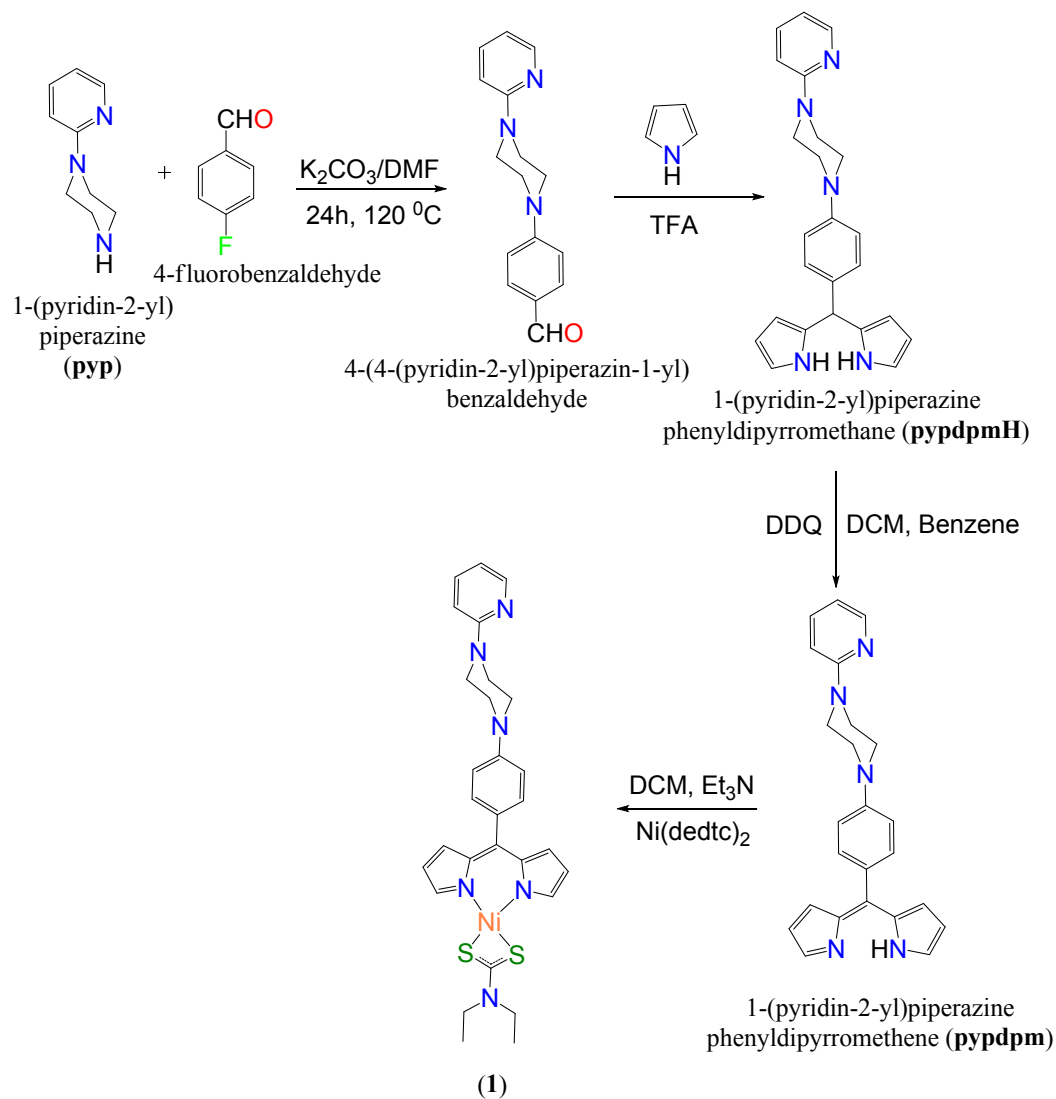
Single crystal X-ray data for **1** was acquired on a R-AXIS RAPID II diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) at single crystal X-ray diffraction center of the National Institute of Advanced Industrial Science and Technology (AIST), Osaka, Japan. The structure was solved by direct methods (SHELXS 97) and refined by full-matrix least squares on F^2 (SHELX 97).¹⁷ All the non-H atoms were treated anisotropically. H-atoms attached to carbon were geometrically fixed and refined using SHELX riding model. Computer program PLATON was used for analysing the interaction and stacking distances.¹⁸ CCDC deposition No. 1057645 (**1**) contains supplementary crystallographic data for this paper. It can be had free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Catalytic Study

Catalytic reduction of aqueous solution of Cr(IV)

To an aqueous solution of K₂Cr₂O₇ (0.2 mM, 3 mL), HCOOH (0.2 mL) and catalysts AuNPs, GO (*c*, 500 mg/mL), AuNPs@prGO100, AuNPs@prGO300 AuNPs@prGO500 (25 μ L, each) were added. After addition of the catalyst, yellow colour of solution turned colorless with increasing reaction time. The progress of reaction was monitored by UV-vis

spectroscopy after intervals. The absorption spectra of the solution were measured in the range of 200-800 nm. Presence of Cr(III) was further established by addition of an excess of NaOH, the colorless solution turned green which characterized the presence of Cr(III) due to the formation of hexahydroxochromate(III).



Scheme S1 Showing synthesis of 4-(4-pyridin-2-yl)piperazin-1-yl)benzaldehyde, 1-(pyridine-2-yl)piperazinephenyldipyrromethane (pypzdpMH), 1-(pyridine-2-yl)piperazine-phenyldipyrromethene (pypzdpM) and heteroleptic complex **1**.

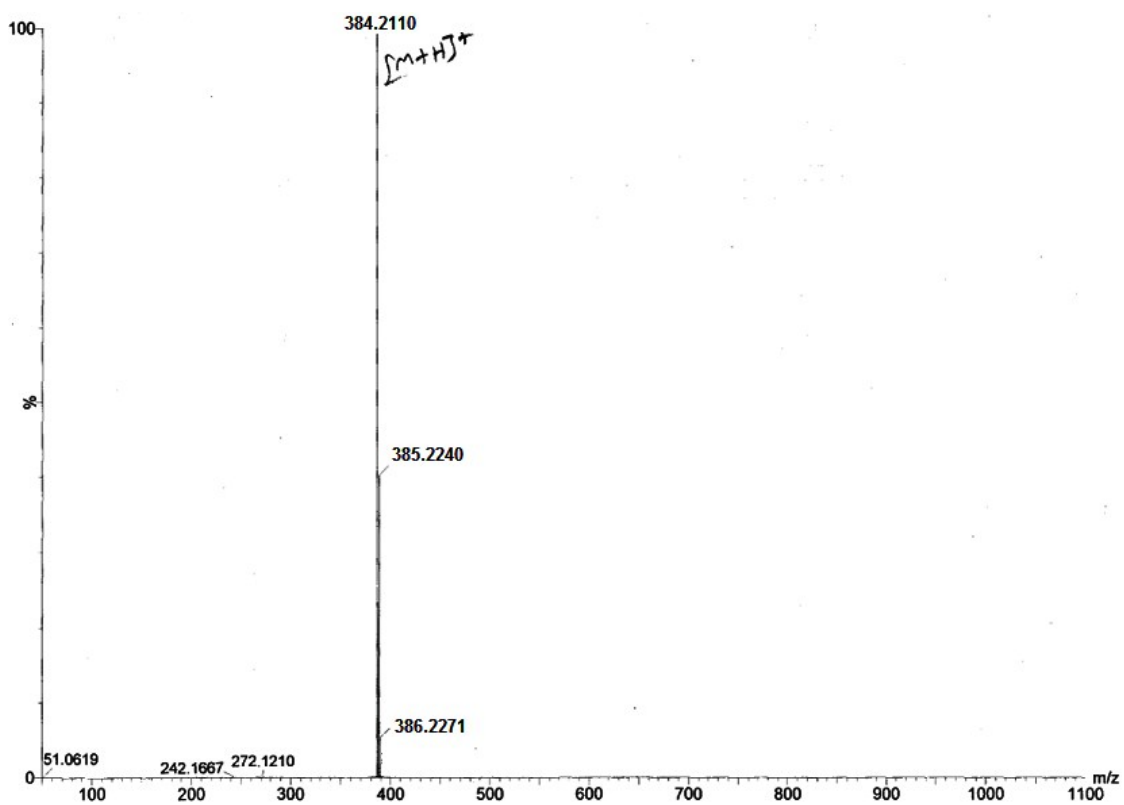


Fig. S1 ESI-MS of pypmdpmH.

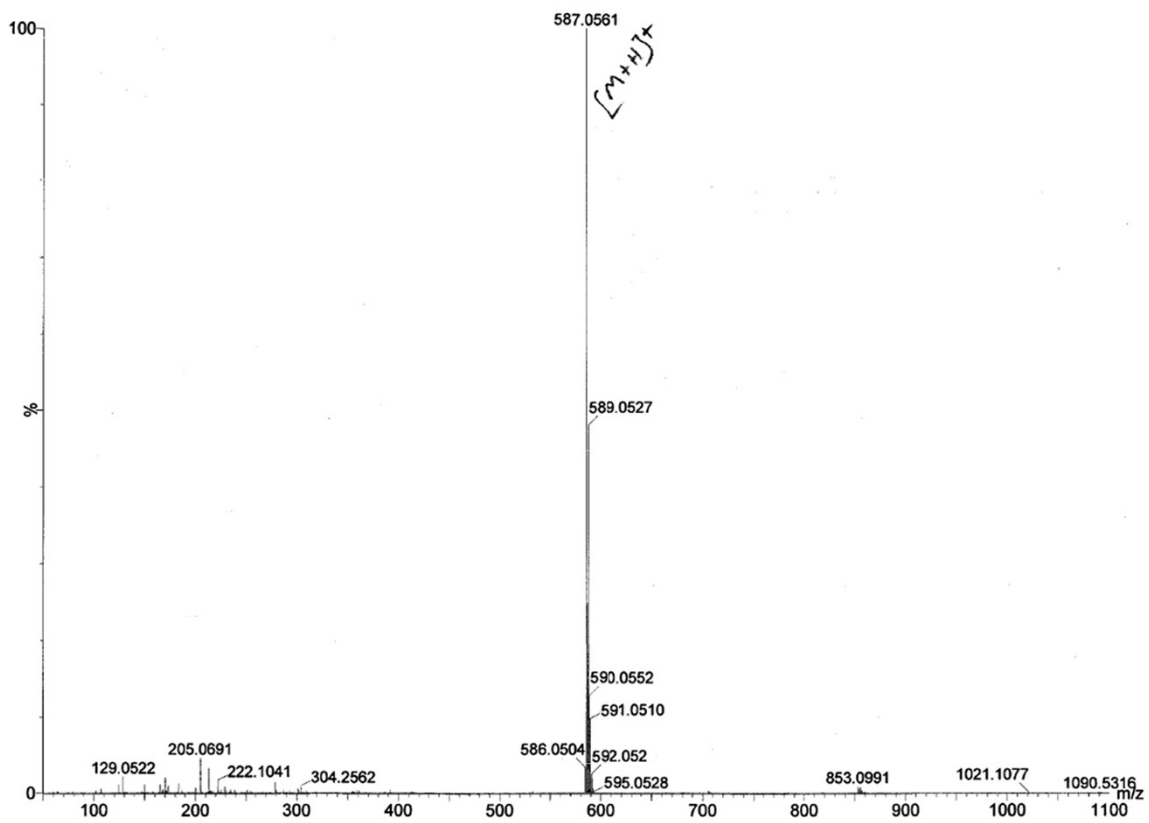


Fig. S2 ESI-MS of complex 1.

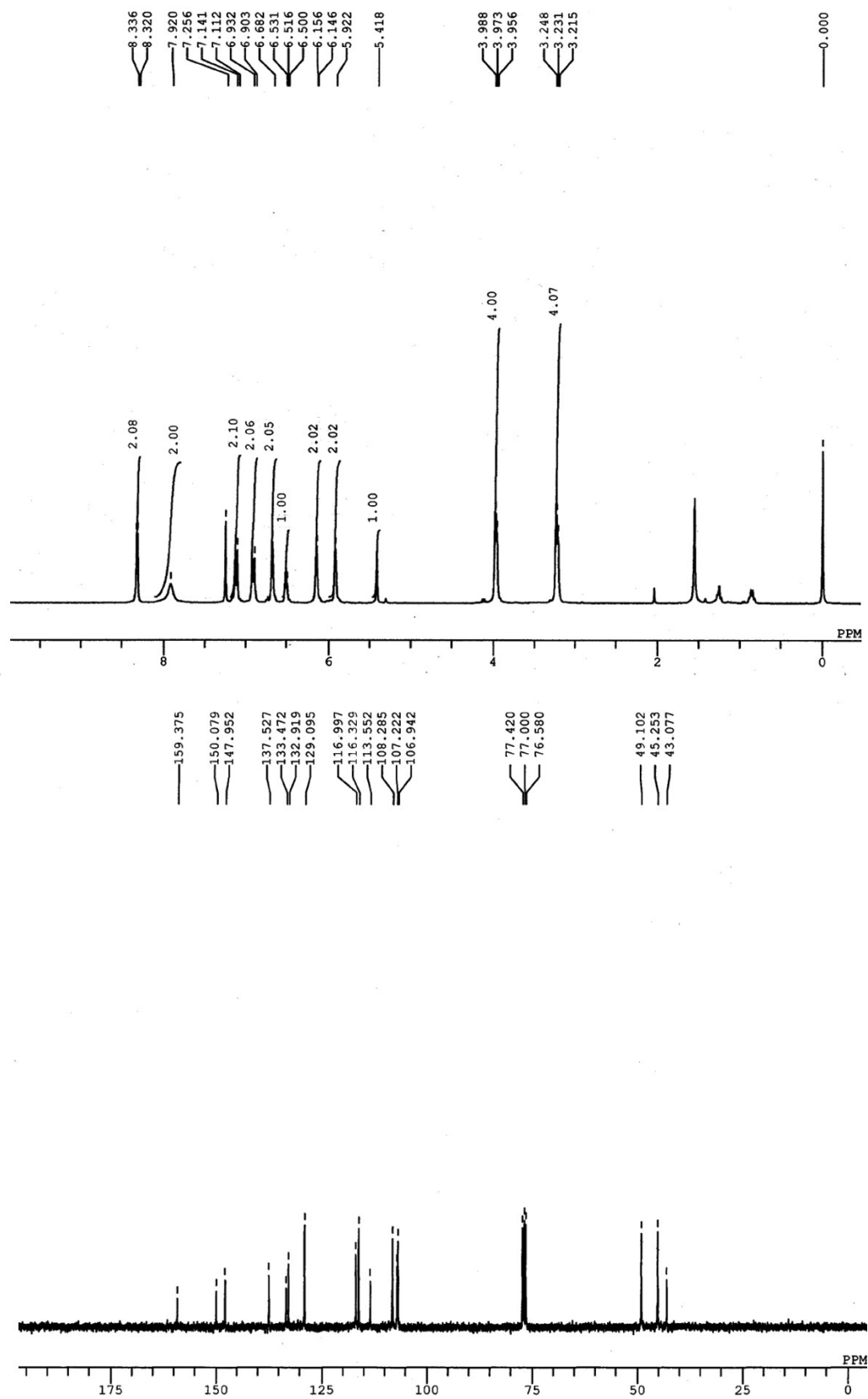


Fig. S3 ¹H (top) and ¹³C NMR (bottom) spectrum of ligand (pypdpmH) in CDCl₃.

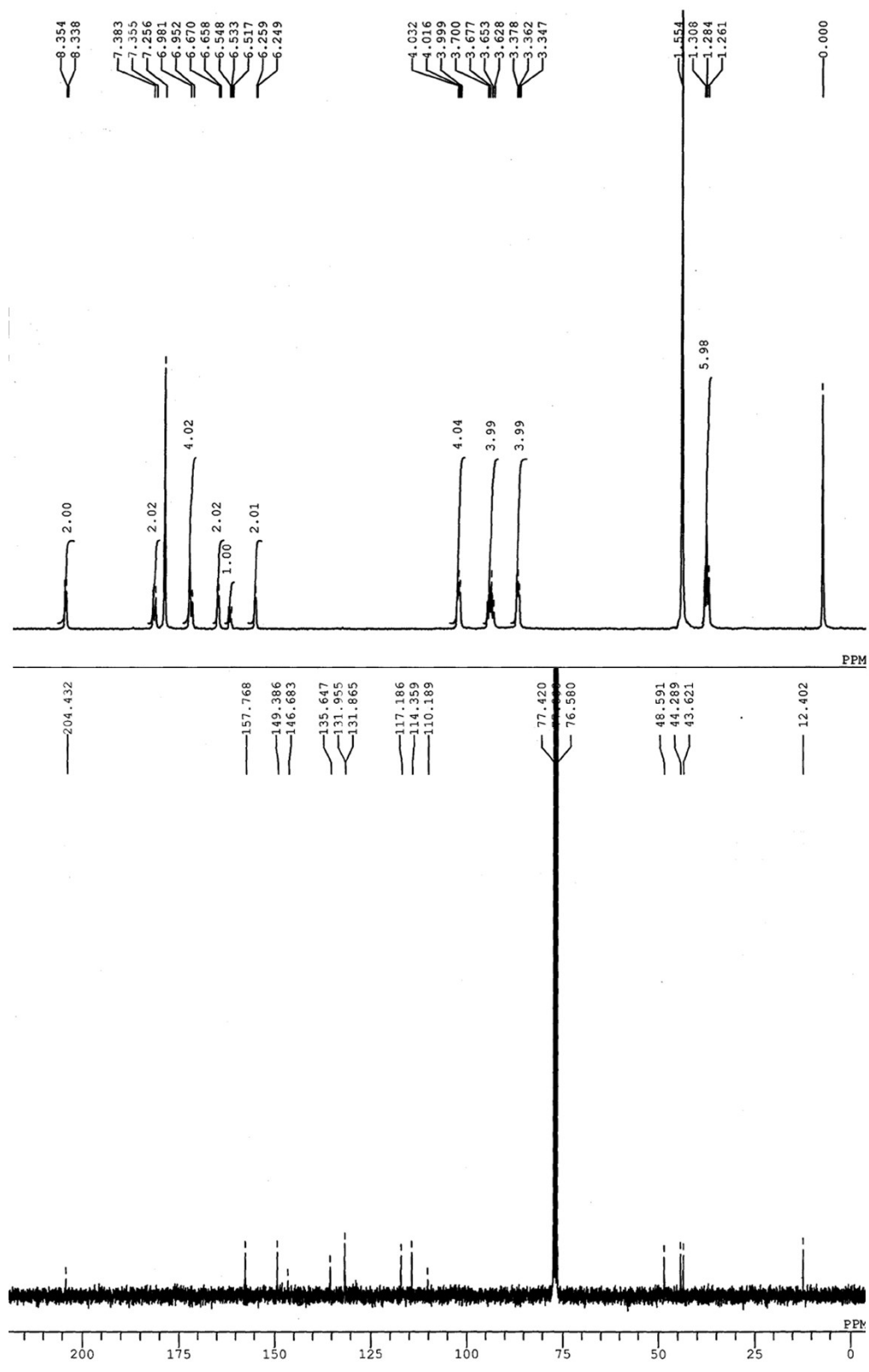


Fig. S4 ¹H (top) and ¹³C NMR (bottom) spectrum of complex (1) in CDCl₃.

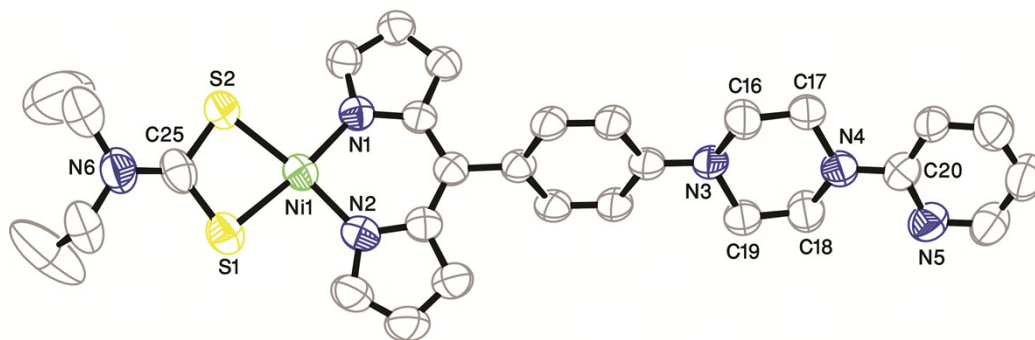


Fig. S5 ORTEP view of **1** at 50% thermal ellipsoid probability (H-atoms omitted for clarity).

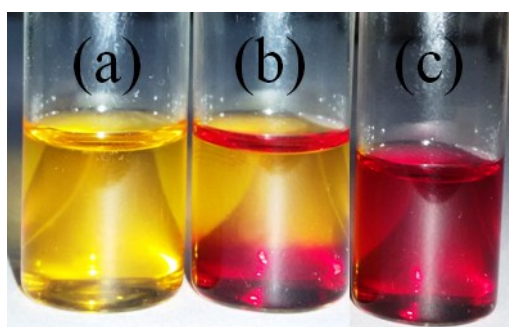


Fig. S6 Colour changes for **1** (a), after addition of HAuCl_4 immediately (b), after shaking (c).

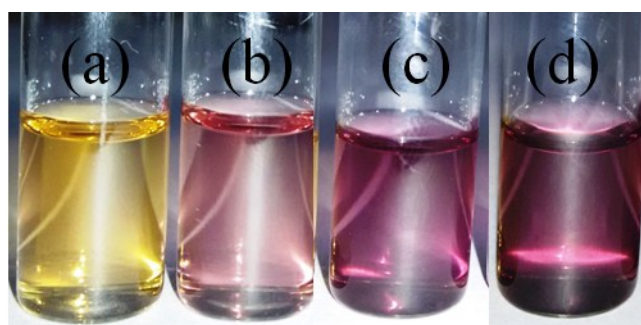


Fig. S7 Colour changes of **pydpmH** (a), after addition of HAuCl_4 5 min (b), 10 min (c) 15 min (d).

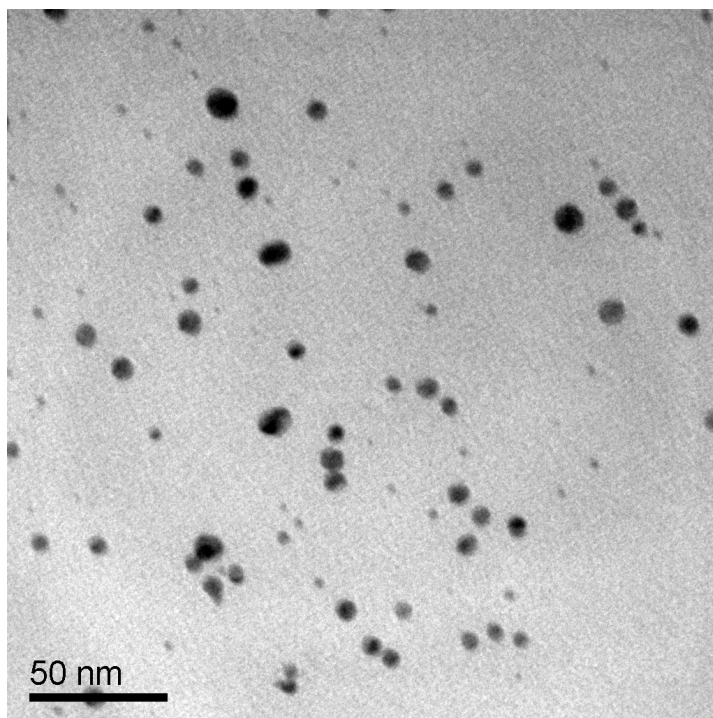


Fig. S8 TEM image of AuNPs synthesized from pydpmH.

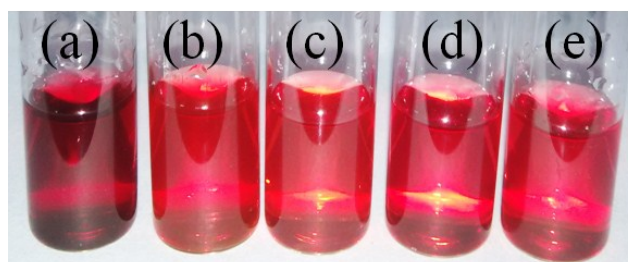


Fig. S9 Colour of AuNPs in methanol (a), ethanol (b) acetonitrile (c), dimethylformamide (d) and dimethyl sulfoxide (e).

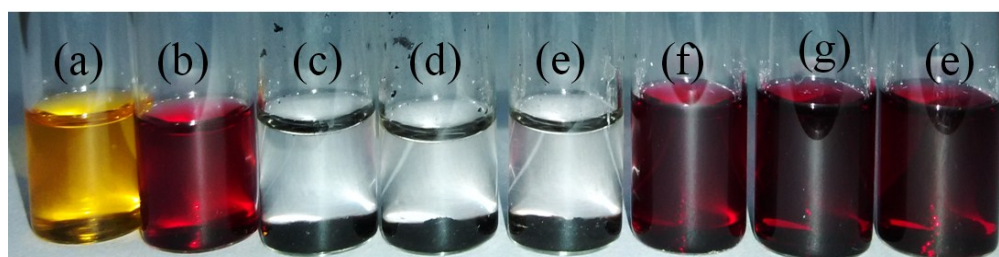


Fig. S10 Colour of **1** (a), AuNPs (b), AuNPs@prGO100 (c), AuNPs@prGO300 (d), AuNPs@prGO500 nanocomposites (e), nanocomposites dissolved in DMF and triple distilled water (5%, v/v) AuNPs@prGO100 (f), AuNPs@prGO300 (g), AuNPs@prGO500 (h).

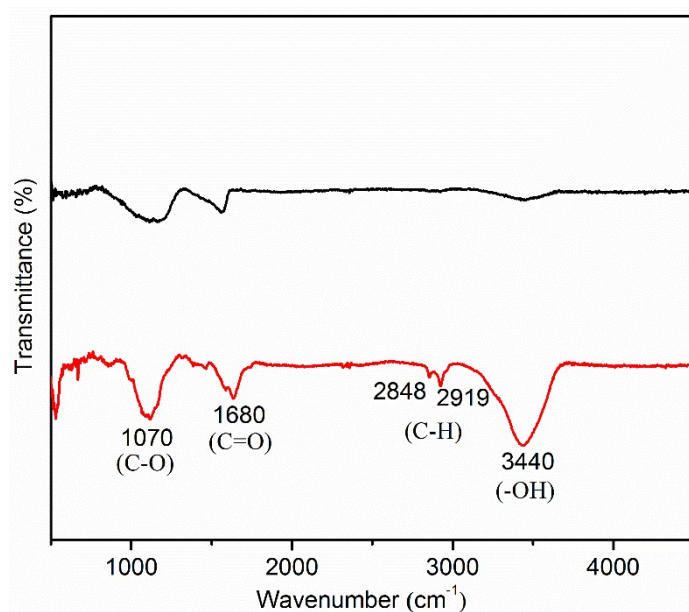


Fig. S11 FTIR spectra of GO (Red Curve) and AuNPs@prGO500 (Black curve)

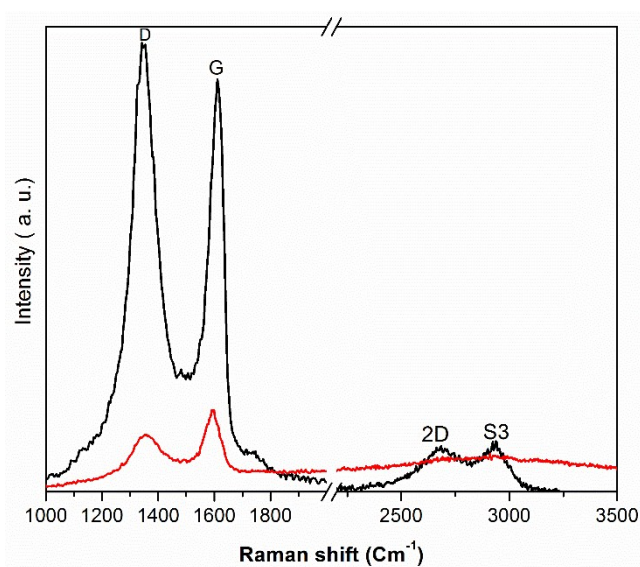


Fig. S12 Raman spectra of GO (red) and AuNPs@prGO500 (black). In AuNPs@prGO500 (after reduction), the intensity ratio I_D/I_G increased significantly than that of GO. In addition, the appearance of prominent 2D and S3 peaks in AuNPs@prGO500 further confirms better graphitization in AuNPs@prGO500.

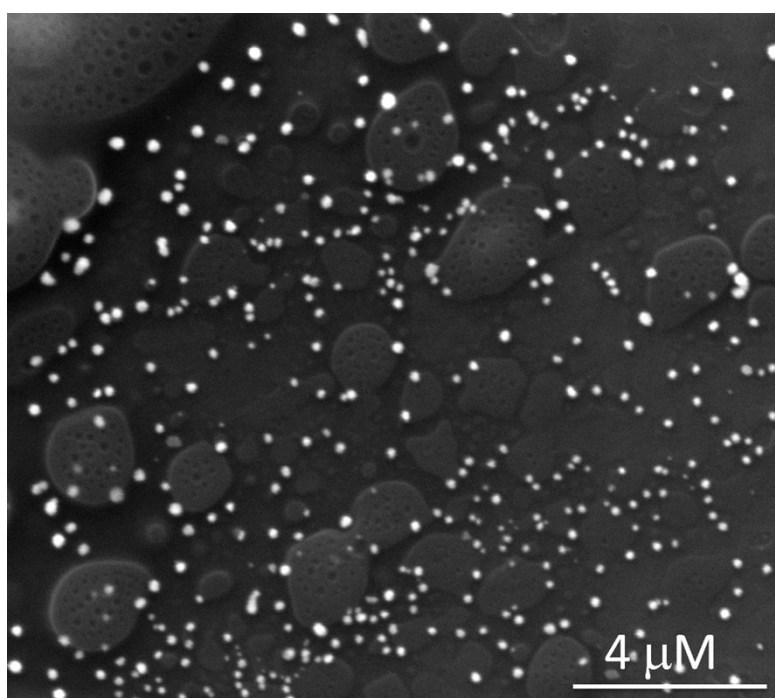


Fig. S13 SEM image of AuNPs synthesized from complex 1.

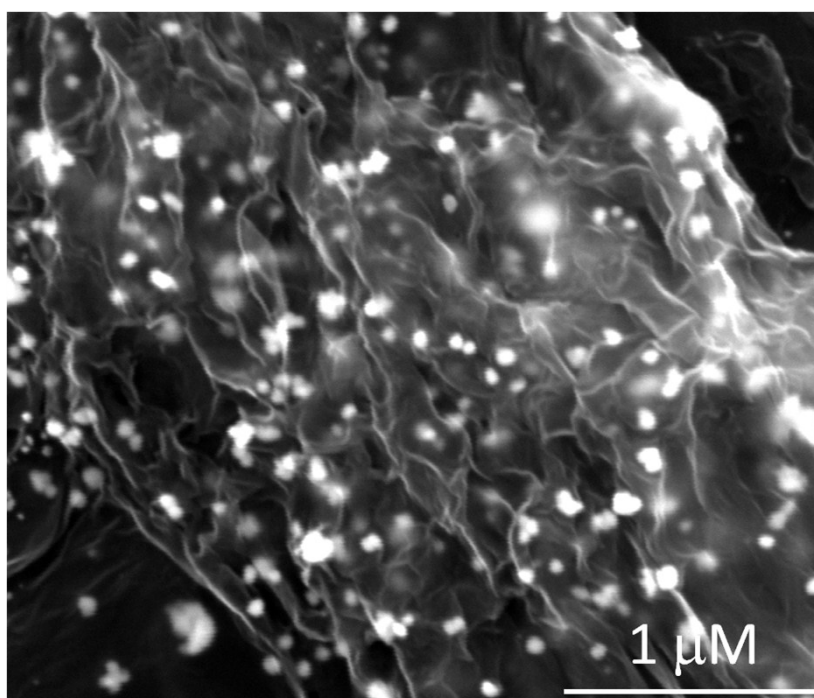


Fig. S14 SEM image of AuNPs@prGO100.

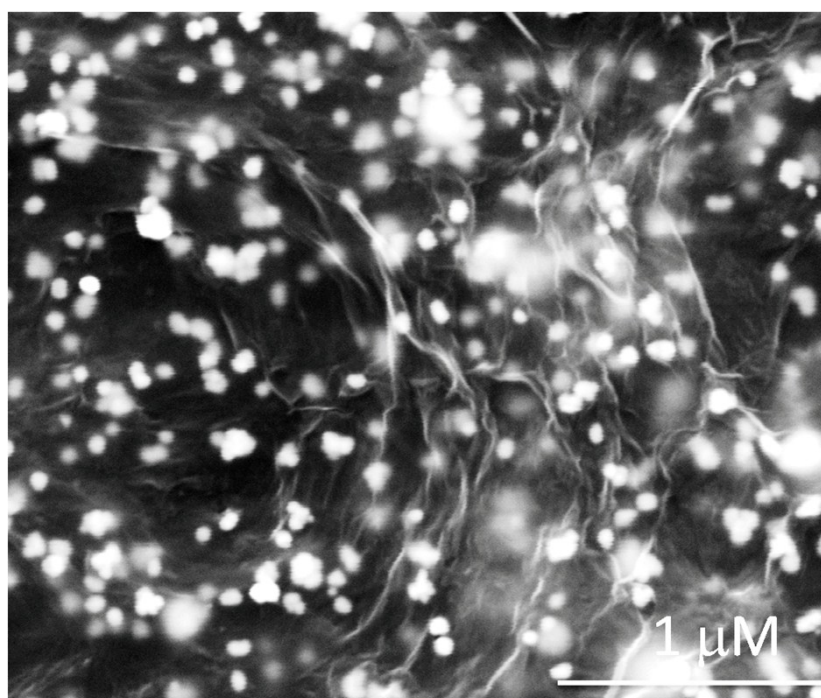


Fig. S15 SEM image of AuNPs@prGO300.

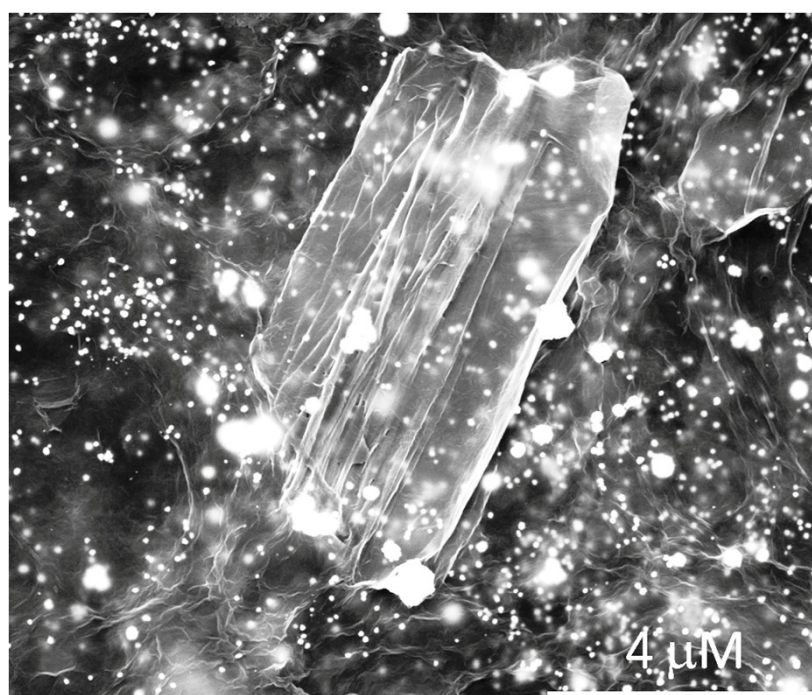


Fig. S16 SEM image of AuNPs decorated on prGO@500.

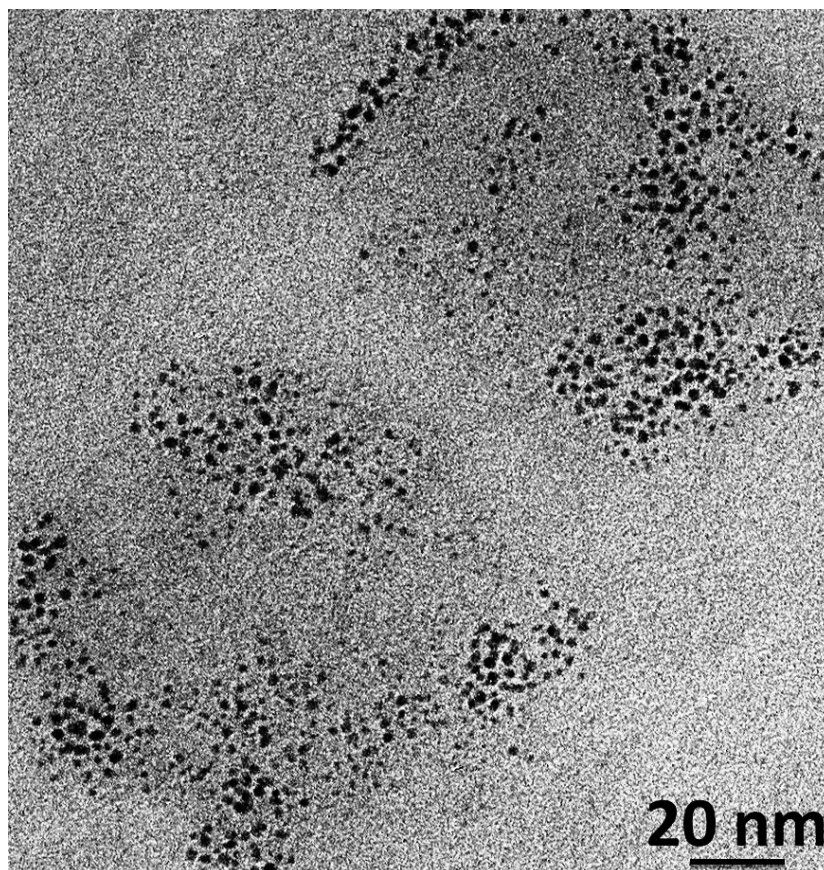


Fig. S17 TEM image of AuNPs.

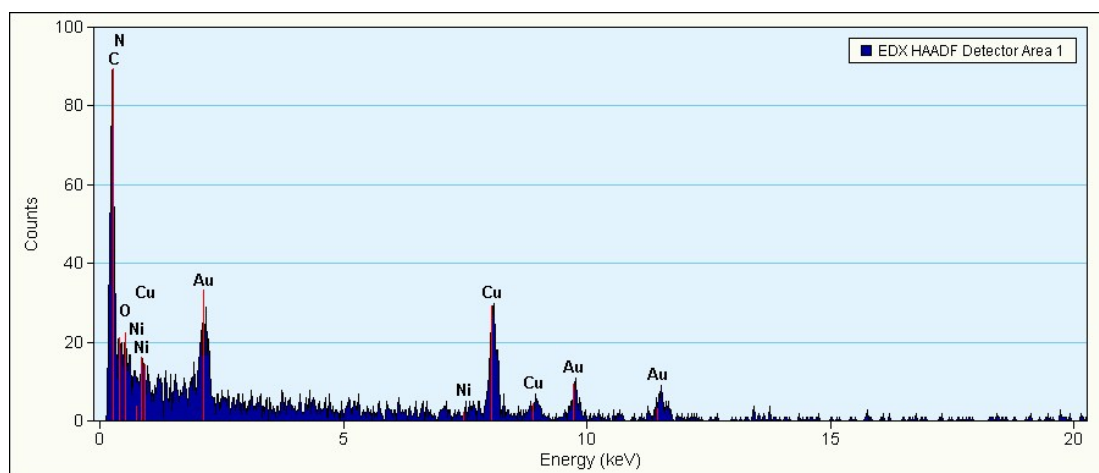


Fig. S18 Energy-dispersive X-ray analysis (EDX) pattern of AuNPs.

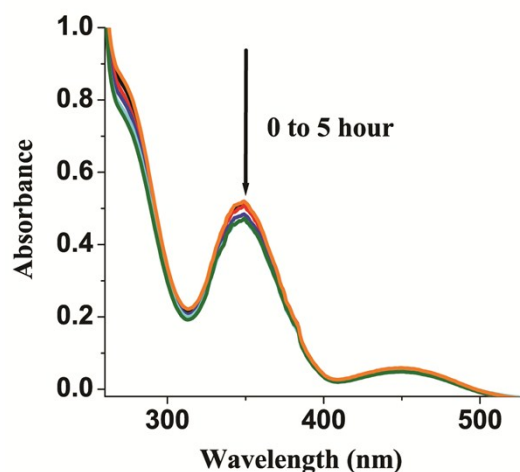


Fig. S19 UV- vis spectra for reductive conversion of Cr(VI) to Cr(III) in dark for 5 hour $[\text{Cr}_2\text{O}_7^{2-}] = 0.2 \text{ mM}$.

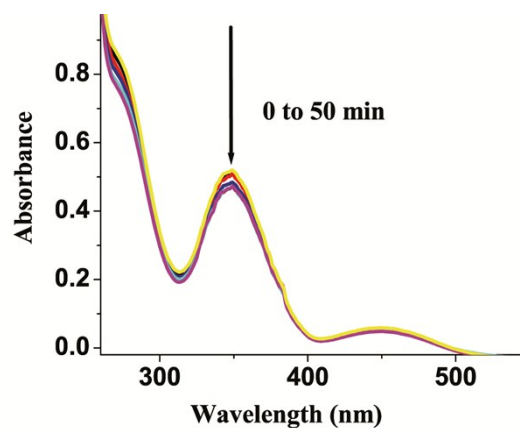


Fig. S20 UV- vis spectra for reductive conversion of Cr(VI) to Cr(III) only in the presence HCOOH. Reaction condition: HCOOH = 0.2 ml, $[\text{Cr}_2\text{O}_7^{2-}] = 0.2 \text{ mM}$.

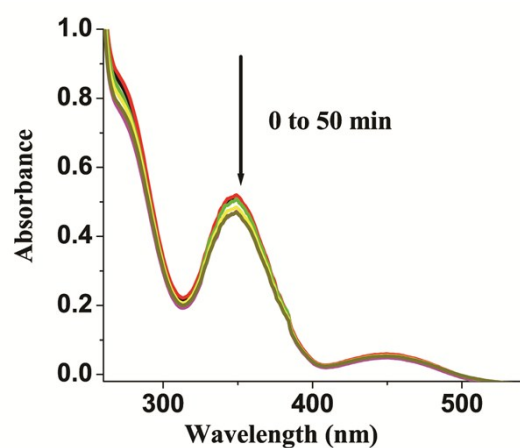


Fig. S21 UV- vis spectra for reductive conversion of Cr(VI) to Cr(III) only in the presence AuNPs@prGO500. Reaction condition: AuNPs@prGO500 = 1 mg/mL (25 μL). $[\text{Cr}_2\text{O}_7^{2-}] = 0.2 \text{ mM}$.

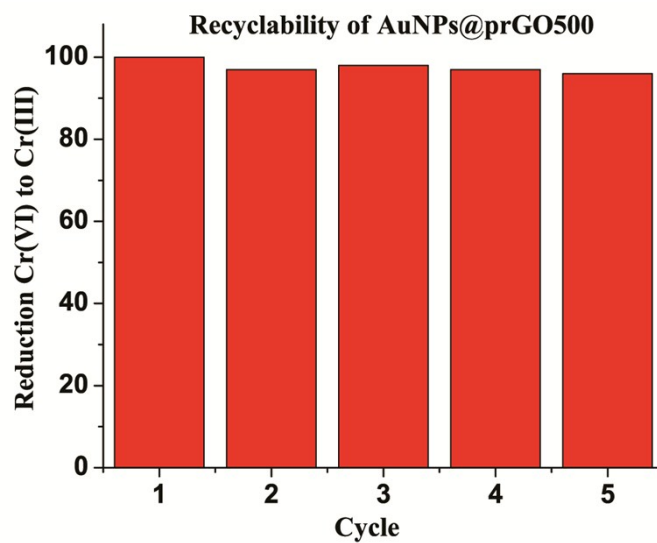


Fig. S22 Recyclability of AuNPs@prGO500 for Cr(VI) to Cr(III) reduction. Reaction conditions: HCOOH = 0.2 mL, $[\text{Cr}_2\text{O}_7^{2-}] = 0.2 \text{ mM}$ and AuNPs@prGO500 = 1 mg/mL (25 μL).

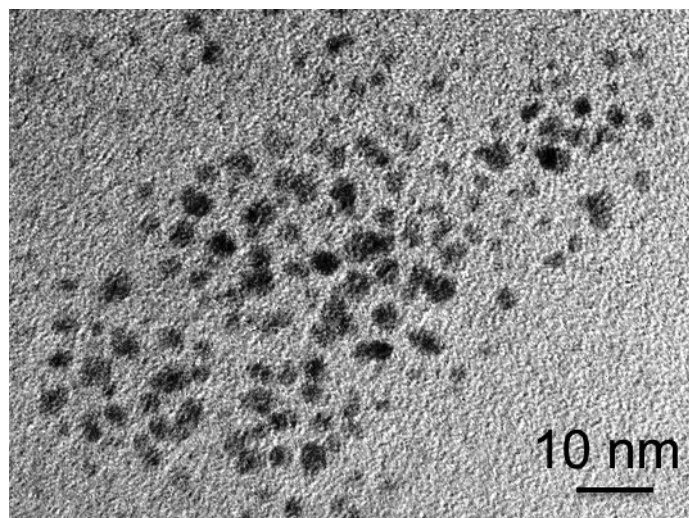


Fig. S23 TEM image of AuNPs@prGO500 after 1st cycle of Cr(VI) reduction.

Table S1 Crystal data and structure refinement parameters for **1**.

Empirical formula	C ₂₉ H ₃₂ N ₆ NiS ₂
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.023(2)
<i>b</i> (Å)	10.298(2)
<i>c</i> (Å)	25.687(5)
α (deg)	90.00
β (deg)	100.50(3)
γ (deg)	90.00
<i>V</i> (Å ³), <i>Z</i>	2867.2(10), 4
λ (Å)	0.71073
Color and habit	Red, needle
<i>T</i> (K)	293(2)
reflns collected	4362
reflins/restraint/params	6584/1/345
<i>D</i> _{calcd} (Mg m ⁻³)	1.361
μ (mm ⁻¹)	0.852
GOF on <i>F</i> ²	1.071
final <i>R</i> indices <i>I</i> >2 σ (<i>I</i>) ^a	R1 = 0.0534
	wR2 = 0.1672
<i>R</i> indices (all data) ^a	R1 = 0.0708
	wR2 = 0.1545

Table S2 Selected bond lengths (Å) and angles (°) for **1**.

Bond length (Å)	1
Ni–N1	1.89(3)
Ni–N2	1.89(3)
Ni–S1	2.20(13)
Ni–S2	2.20(13)
C25–S1	1.70(5)
C25–S2	1.72(4)
C16–N3	1.44(5)
C19–N3	1.44(5)
C17–N4	1.45(5)
C18–N4	1.44(5)
C20–N4	1.36(5)
Bond angle (°)	1
N2–Ni–N1	92.9(13)
N2–Ni–S1	94.0(10)
N1–Ni–S1	173.1(9)
N2–Ni–S2	171.8(10)
N1–Ni–S2	95.1(9)
S1–Ni–S2	78.0(5)
C25–S1–Ni1	86.80(14)
C25–S2–Ni1	86.68(16)
C20–N4–C18	121.3(3)
C20–N4–C17	120.7(3)
C18–N4–C17	114.5(3)
C13–N3–C19	118.6(3)
C13–N3–C16	119.1(3)
C19–N3–C16	113.9(3)
C18–C19–N3	115.5(4)
ω	69.05

ω = the twist angle between dipyrin core and *meso*-phenyl substituent.