

Electronic Supplementary Information (ESI)

Morphology-Tunable Architectures Constructed by

Supramolecular Assemblies of α -Diimine Compound: Fabrication

and Application as Multifunctional Host Systems

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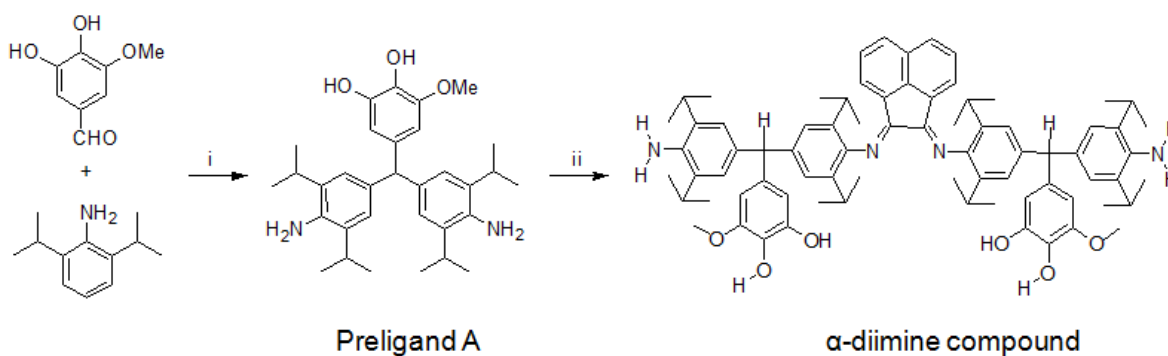
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Experimental

Synthesis of α -diimine compound

The synthetic procedures for α -diimine compound were summarized in Scheme S1. All reactions were performed under a purified nitrogen atmosphere using Schlenk technique. Firstly, preligand A was synthesized by protocol based on the reported procedure for similar compounds.^[S1] 2,6-Diisopropylaniline (4.15 mL, 22 mmol) was heated to 130 °C under inert atmosphere to which 3,4-dihydroxy-5-methoxybenzaldehyde (1.68 g, 10 mmol) dissolved in 10 mL conc. HCl and 40 mL THF (25 mmol batch) were added over a period of 1 h. The reaction mixture was refluxed for 24 h. After cooling to room temperature, it was basified with aq. NaOH and extracted with CHCl₃. The combined organic layers were washed with water and brine respectively. The solution was dried over MgSO₄ and added pentane to precipitate the product. It was purified *via* column chromatography [ethyl acetate/*n*-hexane-silica gel] to afford the product as pure reddish brown powder (yield = 40 %, 2.02 g). ¹H-NMR (300 MHz, CDCl₃) δ 1.25 (d, 24 H, CH₃^{ipr}), 2.98 (sep, 4 H, CH^{ipr}), 3.71 (s, 3 H, OCH₃), 4.11 (s, 4 H, NH₂), 5.30 (s, 1 H, CH), 6.75 (d, 2 H, H_{arom}), 7.10 (s, 2 H, H_{arom}), 7.20 (s, 2 H, H_{arom}), 12.2 (s, 2 H, OH); ¹³C-NMR (75 MHz, CDCl₃) δ 23.42, 27.45, 56.63, 58.78, 117.04, 118.58, 127.95, 129.73, 132.28, 135.75, 138.42, 146.06, 149.56. Anal. Calcd for C₃₂H₄₄N₂O₃: C, 76.15; H, 8.79; N, 5.55. Found: C, 76.20; H, 8.85; N, 5.56.



Scheme S1. Synthesis of ligands: (i) HCl, THF; (ii) Acenaphthenequinone, MeOH;/ H⁺.

To synthesize α -diimine compound, a methanol solution of the pre-ligand **A** (8 mmol, 4.03 g), acenaphthenequinone (4 mmol, 0.73 g) was added in 2:1 ratio and a catalytic amount of formic acid. The reaction mixture was stirred overnight at room temperature. After the reaction, methanol was removed under vacuum and the resulting product was purified *via* column chromatography [ethyl acetate/*n*-hexane-silica gel]. The solvent was evaporated and dried at 60 °C under vacuum to get α -diimine complex in 62 % (2.87 g) yield. ¹H-NMR (300 MHz, CDCl₃) δ 1.25-1.37 (dd, 48 H, CH₃^{ipr}), 3.15 (m, 8 H, CH^{ipr}), 3.90 (s, 6 H, OCH₃), 4.12 (s, 4 H, NH₂), 5.24 (s, 2 H, CH), 6.64-7.12 (m, 8 H, H_{arom}), 7.34 - 7.56 (m, 6 H, H_{arom}), 7.56 - 7.75 (4 H, H_{arom}), 12.5 (s, 4 H, OH); ¹³C-NMR (300 MHz, CDCl₃) δ 23.47, 23.75, 28.90, 29.76, 55.88, 56.66, 115.92, 123.51, 124.82, 126.21, 128.85, 129.32, 129.82, 130.14, 130.82, 131.12, 131.74, 132.12, 33.16, 135.21, 138.21, 141.82, 146.23, 157.51, 163.75. Anal. Calcd for C₇₆H₉₀N₄O₆: C, 78.99; H, 7.85; N, 4.85. Found: C, 79.02; H, 7.92; N, 4.87.

Molecular dynamics simulations and polymorph prediction

Molecular mechanics calculations were performed using Materials Studio[®] 4.3.^[S2] For all solid-state simulations, the Ewald method^[S3,S4] was used for the electrostatic and van der Waals interaction terms. Gasteiger charges were used for an initial conformational search. Subsequent calculations used electrostatic potential derived charges.

As the crystal structure prediction method uses a rigid body approximation in the initial search for crystal packing alternatives, it is necessary to perform an analysis to determine low energy geometry to be used as input for the packing calculations. The molecules were drawn and geometrical energy minimization scans were performed using Forcite module of Materials Studio (Fig. S1 and Table S1). The compound **3** in Fig. S1 was found to have the lowest energy conformation (Table S1). The force field used was Dreiding 2.21^[S5] with Gasteiger charges (as implemented in the Materials Studio packages). Initially geometry optimization was performed by using Smart algorithm in Forcite module of Materials Studio (convergence tolerance energy of 2×10^{-5} kcal/mol, force of 0.001 kcal/mol/Å, and

displacement of 1×10^{-5} Å with maximum number of iterations of 500 for an independent optimization) in the microcanonical ensemble (NVE). The optimized low energy conformations were reoptimized by a molecular dynamics simulation using the same module (simulation length of 5 ps with a 1 fs time step at a temperature of 298 K, taking conformations every 5000 steps). These optimized gas phase conformations were used as the starting points for crystal structure prediction using the Materials Studio Polymorph Predictor (PP).^[S2] The optimized structure of **3** (Fig. S1) was used for PP calculation.

The PP was set to its default fine setting (this sets the simulated annealing algorithm to a temperature range of 300-100000.0 K with a heating factor of 0.025, requiring 12 consecutive steps to be accepted before cooling and a maximum of 7000 steps) with the force field Dreiding 2.21 with Gasteiger charges. The 10 most common space groups^[S6] found in organic crystals registered in the CSD were selected (*P2₁/c*, *P1*, *P2₁2₁2₁*, *P2₁*, *C2/c*, *Pbca*, *Pna2₁*, *Pbcn*, *Cc*, and *C2*). Clustering of the predicted polymorphs was done using the polymorph clustering routine in Materials Studio, combined with a spreadsheet macro. The Materials Studio polymorph clustering routine was unable to cluster all the polymorphs generated in this investigation within a reasonable amount of disk space and time. Therefore, the routine was only used to cluster all the polymorphs for each conformation used in the prediction. An Excel macro was written which compares the lattice energy and density for each crystal structure, and this macro was subsequently used to cluster the unique polymorphs obtained for the different conformations. The polymorph predictions were repeated four times for each starting conformation to ensure adequate sampling of the crystal configurations. After geometry optimization, the density of ligand and Ni(II) complex crystal structures reaches 0.6–1.05 and 0.75–1.28 g cm⁻³ (see Figure S2). After a final clustering, the calculated crystal structures were ranked on the one hand according to their total energy and on the other hand according to their density. At least 20 structures with low energy and 20 structures with high density were also compared ‘by eye’ attempting to identify the packing motifs.

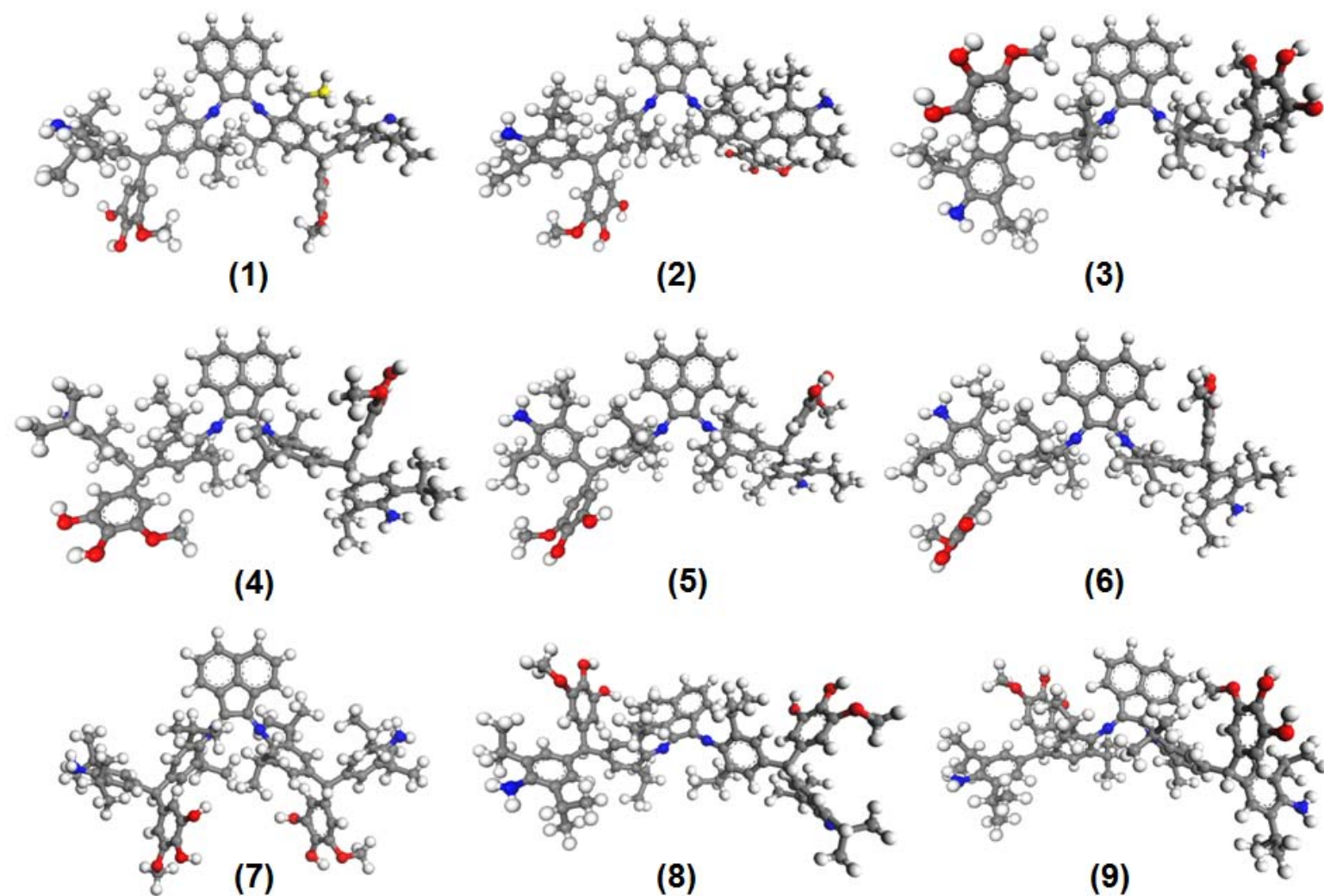


Figure S1. The molecular and geometry-optimized structures of different DC configurations; the energy minimization scans were performed using Forcite module of Materials Studio[®] 4.3 to achieve optimized gas phase geometry.

Table S1. Energy details of different DC configurations in Figure S1 obtained from the simulation results.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	kcal/mol	kcal/mol	kcal/mol	kcal/mol	kcal/mol	kcal/mol	kcal/mol	kcal/mol	kcal/mol
Valence energy (diag. terms)	75.992	46.137	41.272	48.571	57.607	62.029	62.933	73.949	71.048
Bond	27.498	21.577	20.903	21.050	21.453	21.024	21.457	21.662	19.027
Angle	83.345	59.653	64.005	68.043	70.198	70.529	68.059	64.859	65.163
Torsion	-39.032	-37.476	-45.243	-42.334	-36.197	-32.045	-29.850	-17.481	-17.895
Inversion	4.182	2.382	1.607	1.812	2.153	2.521	3.267	4.909	4.753
Valence energy (cross terms)	-31.741	-32.223	-30.745	-31.625	-31.770	-32.035	-33.013	-33.850	-29.730
Stretch-Stretch	1.324	1.614	1.480	1.643	1.607	1.565	1.694	1.809	1.407
Stretch-Bend-Stretch	-1.993	-1.279	-1.769	-1.169	-0.964	-1.192	-1.643	-0.780	-1.002
Stretch-Torsion-Stretch	-8.975	-9.778	-9.536	-9.532	-9.713	-9.381	-9.932	-9.890	-9.413
Separated-Stretch-Stretch	0.953	1.258	1.196	1.213	1.193	1.207	1.374	1.386	1.086
Torsion-Stretch	-31.762	-35.019	-33.983	-34.727	-34.510	-34.487	-35.392	-36.592	-31.993
Bend-Bend	-0.097	-0.268	-0.368	-0.542	-0.409	-0.465	-0.150	-0.206	-0.103
Torsion-Bend-Bend	-1.843	-0.804	-0.995	-1.203	-1.107	-1.332	-0.873	-0.865	-0.940
Bend-Torsion-Bend	10.652	12.054	13.229	12.693	12.132	12.050	11.908	11.287	11.229
Non-bond energy	23.249	11.743	12.770	10.892	12.515	14.743	10.707	16.162	12.854
Hydrogen bond	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
van der Waals	46.134	42.134	38.616	40.575	43.309	40.240	38.108	38.130	37.014
Electrostatic	-22.885	-30.392	-25.845	-29.683	-30.794	-25.497	-27.401	-21.968	-24.160
3-Body	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total energy	67.500	25.656	23.298	27.839	38.351	44.736	40.627	56.260	54.172

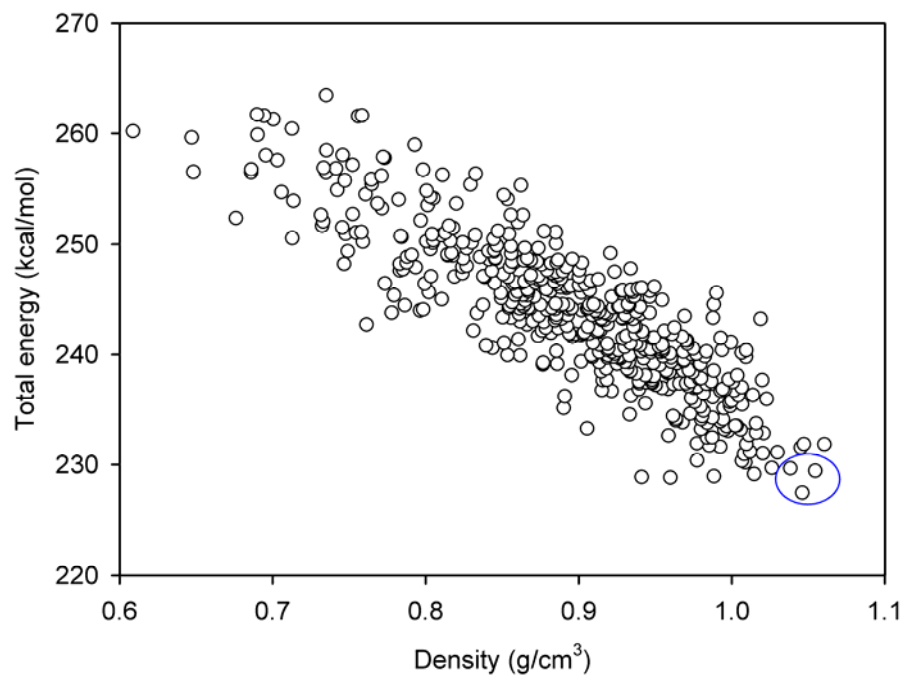


Figure S2. Energy-density plot in the space groups $P2_1/c$, $P1$, $P2_12_12_1$, $P2_1$, $C2/c$, $Pbca$, $Pna2_1$, $Pbcn$, Cc , and $C2$ (by Materials Studio Polymorph Predictor): (a) packing by using compound **3** in Figure S1. The circled points are corresponding to $P1$ packing.

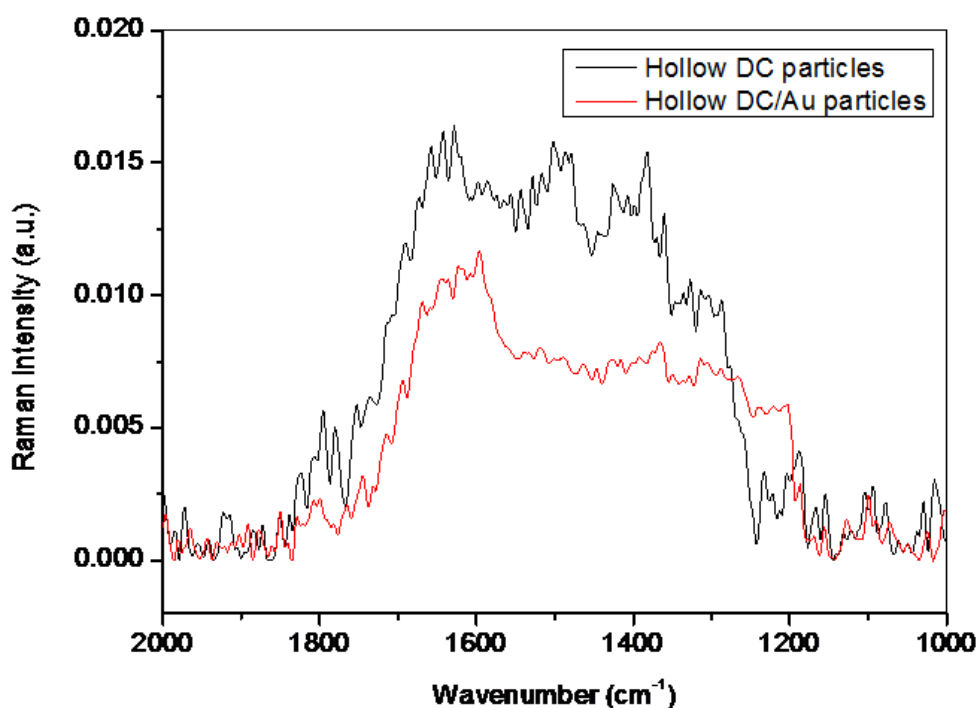


Figure S3. Raman spectra of self-assembled DC hollow spheres and hollow DC/Au solid spheres obtained by two-step reaction.

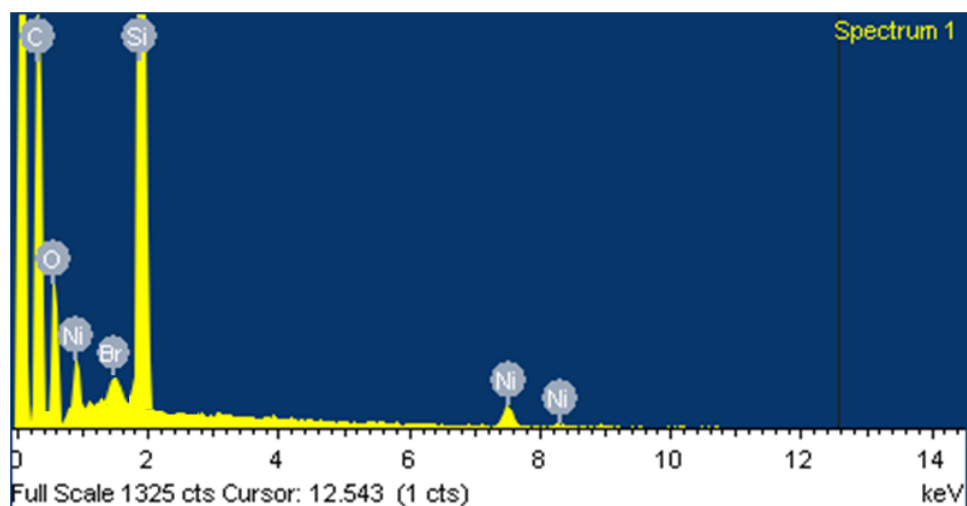


Figure S4. EDS spectra of Ni(II) coordinated hollow DC self-assembled particles. No nitrogen signal is presented since it is difficult to detect light elements by EDS analysis.

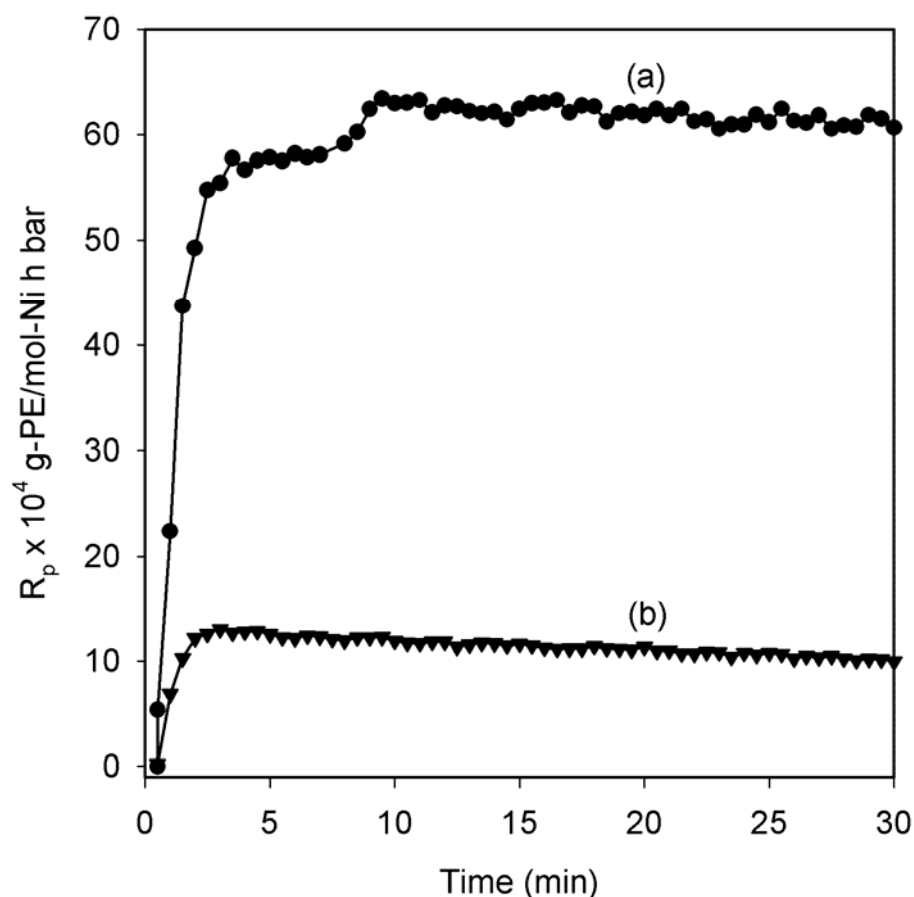


Figure S5. Rate of polymerization (R_p) versus time plot of ethylene polymerization by catalyst precursor: a) hollow DC sphere/MAO, b) solid DC sphere /MAO. Polymerization conditions: toluene solvent = 80 mL in a 250 mL glass reactor, temperature = 50 °C, catalyst = 2.5 μmol , Al/Ni = 250 and atmospheric pressure of monomer.

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