Supporting Information

Visible-Light-Induced Controlled Radical Polymerization of Methacrylates Mediated by Pillared-Layer Metal-Organic Framework

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Materials

Zinc chloride (ZnCl$_2$, 98% purity, Tianjin Fuchen), terephthalic acid (C$_8$H$_6$O$_4$, 99%, Tianjin Heowns Biochem LLC), N, N-dimethylformamide (DMF, 99.8%, Tianjin Guangfu), hydrochloric acid (HCl, 36%~38%, Beijing Chemical Works), anthracene (C$_{14}$H$_{10}$, 98%, Tianjin Guangfu), 4-ethynlypyridine hydrochloride (C$_7$H$_5$N•HCl, 95%, Bepharm Limited), bis(triphenylphosphine)palladium(II) dichloride (Pd 15.2%, Aladdin), copper (I) iodide (CuI, 99.5%, Sinopharm Reagent Co., Ltd), ethyl α-bromoisobutyrate (EBiB, 99%, Accela), copper(II) bromide (CuBr$_2$, 99%, Acros). N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, 99%, TCI) and acetonitrile (CH$_3$CN, 99.9%, Acros) were used as received without any further purification. Triethylamine was prepared according to literature procedures and all other reagents were obtained from commercial sources and used as received.

Synthesis of L$_1$

The synthesis of the anthracene derivative pillaring ligands was performed with Sonogashira reaction as the key step. In this process a coupling reaction between a terminal alkyne and a halogenated aromatic compound is effected. Typically, a mixture of 9,10-dibromoanthracene (1.008 g, 3.0 mmol), 4-ethynlypyridine hydrochloride (1.089 g, 7.8 mmol) and PdCl$_2$(PPh$_3$)$_2$ (0.211 g, 10 mol %) was dissolved in the dry anaerobic triethylamine/DMF solution (1:1, 40 ml) in a round-bottom flask. The solution was allowed to stir for 10 min at room temperature and CuI (0.171 g, 30 mol %) was subsequently added. A stream of nitrogen was bubbled through the reaction system for about 1h in order to free it from air and the solution was heated to 85 °C under reflux for one day in the nitrogen-filled environment. Then the solvents were removed with a rotary evaporator and the residue was dissolved in dichloromethane, filtered and purified on a silica column with a 1:1 mixture of ether:
ethyl acetate as the eluent. Orange solid of the ligand (0.330 g) were finally isolated (about 30% yield, on the basis of 4-ethynylpyridine hydrochloride). $^{1}$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.63 (4H, d, $J = 6$ Hz, PyH), 7.71 (4H, m, ArH), 8.66 (4H, m, PyH), 8.73 (4H, d, $J = 6$ Hz, PyH). IR (KBr)/ cm$^{-1}$: $\tilde{\nu} = 3036$ (Arom. CH), 2205 (C≡C), 1733, 1588–1403 (Ar), 826 (4-monosubst. pyridine).

**Structure determination**

Diffraction intensity data were collected on an Oxford Diffraction Xcalibur Eos diffractometer with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). All data were collected at a temperature of 150 K. The structures were solved by the direct methods and refined on $F^2$ by full-matrix least-squares using the SHELXTL-97 program.$^3$ The Zn$^{2+}$ ion was easily located and then non-hydrogen atoms (O, N and C) were placed from the subsequent Fourier-difference maps. A summary for data collection and refinements were given in Table S1.
Table S1 Crystal data and structural refinement for NNU-35.

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<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>empirical formula</td>
<td>C$<em>{75}$ H$</em>{47}$ N$_5$ O$_9$ Zn$_2$</td>
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<tr>
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<tr>
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<td>Reflections collected / unique</td>
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<td>data / restraints / parameters</td>
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<td>R(int)</td>
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<td>goodness-of-fit on $F^2$</td>
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<td>Final R indices ([I &gt; 2σ(I)])</td>
<td>$R_1 = 0.1421$, $wR_2 = 0.3663$</td>
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<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.2260$, $wR_2 = 0.4121$</td>
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</table>
Fig. S1 (a) Coordination arrangements of zinc dimmers; (b) Two-fold interpenetration structure of NNU-35. Blue, green, pink, and orange spheres/polyhedra represent zinc, oxygen, nitrogen and carbon atoms, respectively. All hydrogen atoms were omitted for clarity.
Fig. S2 TGA curve of NNU-35.
Fig. S3 PXRD patterns of NNU-35. (a) simulated X-ray pattern from crystal structure; (b) PXRD pattern of the as-synthesized crystalline sample; (c) NNU-35 after photocatalysis reaction.
Fig. S4 In situ time-evolution EPR spectra of pillaring ligand L₁ in solid state under visible light.
Fig. S5 UV-vis spectrum for the ATRP reaction without NNU-35.
Fig. S6 IR spectrum of NNU-35.
Fig. S7 The reuse of NNU-35 to initiate the visible-light-induced polymerization of MMA. \([\text{MMA}]_o/\text{[EBiB]}_o/\text{[CuBr}_2]_o/\text{[PMDETA]}_o = 200/1/0.2/0.6\) in 2mL acetonitrile, NNU-35 = 20 mg, irradiation time = 14 h.

References:

