

Supporting Information

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

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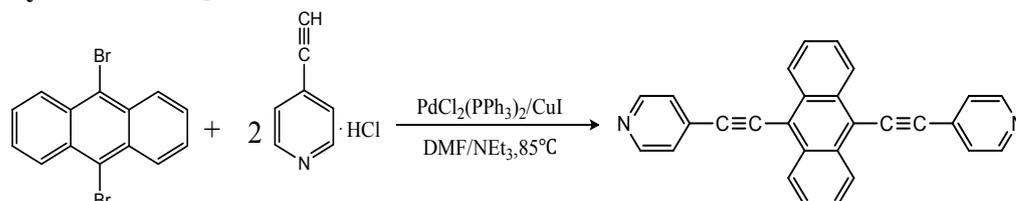
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Materials

Zinc chloride (ZnCl_2 , 98% purity, Tianjin Fuchen), terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$, 99%, Tianjin Heowns Biochem LLC), N, N-dimethylformamide (DMF, 99.8%, Tianjin Guangfu), hydrochloric acid (HCl, 36%~38%, Beijing Chemical Works), anthracene ($\text{C}_{14}\text{H}_{10}$, 98%, Tianjin Guangfu), 4-ethynylpyridine hydrochloride ($\text{C}_7\text{H}_5\text{N}\cdot\text{HCl}$, 95%, Bepfarm Limited), bis(triphenylphosphine)palladium(II) dichloride (Pd 15.2%, Aladdin), copper (I) iodide (CuI, 99.5%, Sinopharm Reagent Co., Ltd), ethyl α -bromoisobutyrate (EBiB, 98%, Accela), copper(II) bromide (CuBr_2 , 99%, Acros). N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, 99%, TCI) and acetonitrile (CH_3CN , 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.^{1, 2} 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-ethynylpyridine hydrochloride (1.089 g, 7.8 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (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). ¹H NMR (500 MHz, CDCl₃, δ): 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 K α radiation (λ = 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 Zn²⁺ 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.

empirical formula	$C_{75} H_{47} N_5 O_9 Zn_2$
formula weight	1292.96
crystal system	monoclinic
space group	$C2/c$
$a / \text{\AA}$	28.525
$b / \text{\AA}$	29.966
$c / \text{\AA}$	14.784
β / degree	109.02
$V / \text{\AA}^3$	11947.1
Z	8
F(000)	5096
θ range collected / degree	3.11 to 27.10
limiting indices	$-36 \leq h \leq 36, -32 \leq k \leq 37, -18 \leq l \leq 18$
Reflections collected / unique	33906 / 12815
data / restraints / parameters	12815 / 38 / 821
$R(\text{int})$	0.1054
goodness-of-fit on F^2	1.085
Final R indices ($[I > 2\sigma(I)]$)	$R_1 = 0.1421, wR_2 = 0.3663$
R indices (all data)	$R_1 = 0.2260, wR_2 = 0.4121$

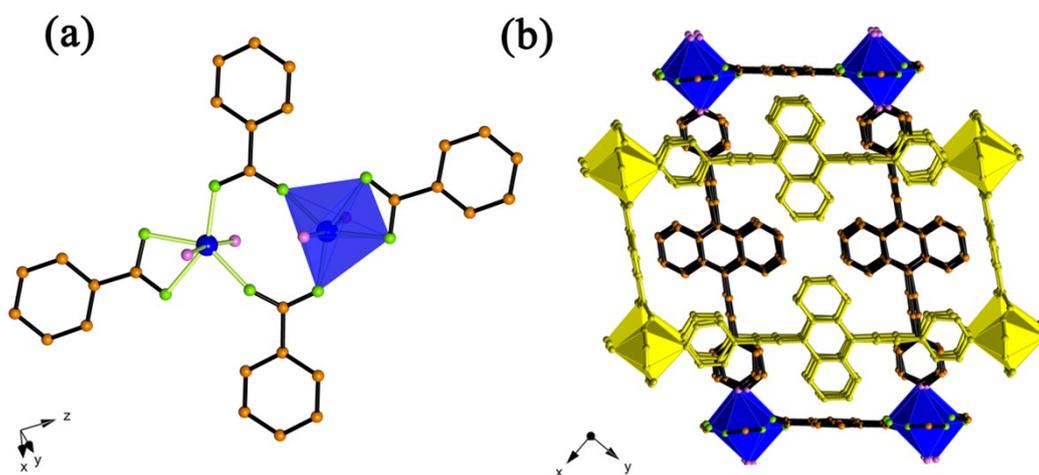


Fig. S1 (a) Coordination arrangements of zinc dimmers; (b) Two-fold interpenetration structure of NNU-35. Blue, green, pink, and orange spheres /polyhedra represent zinc, oxygen, nitrogen and carbon atoms, respectively. All hydrogen atoms were omitted for clarity.

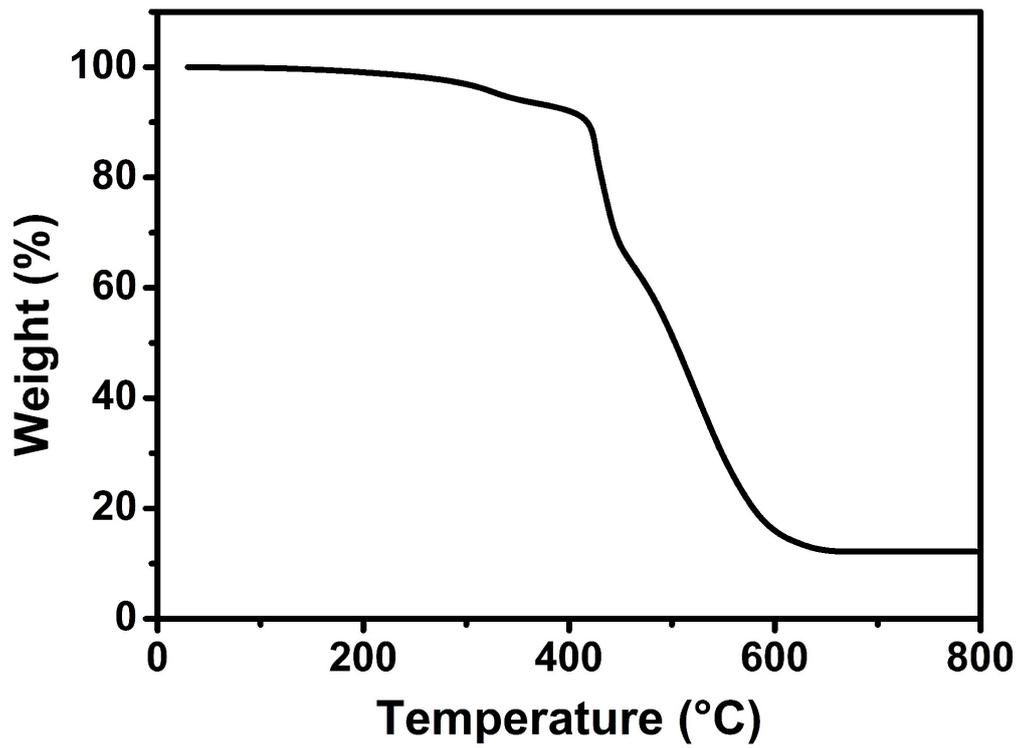


Fig. S2 TGA curve of NNU-35.

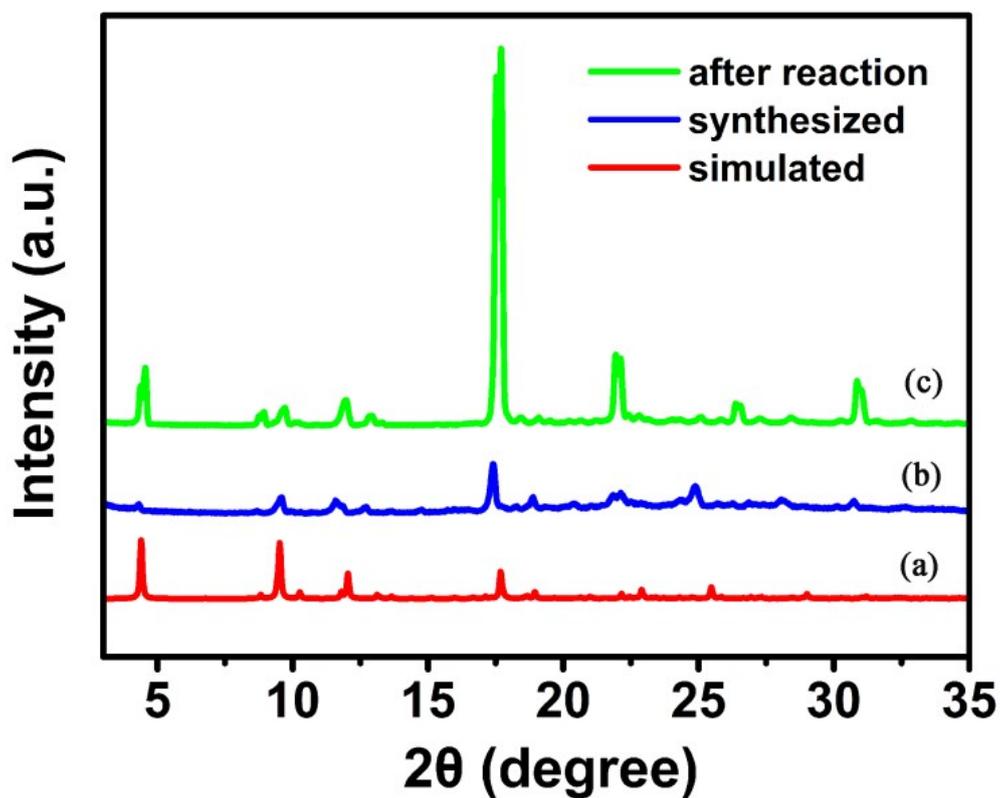


Fig. S3 PXRd patterns of NNU-35. (a) simulated X-ray pattern from crystal structure; (b) PXRd pattern of the as-synthesized crystalline sample; (c) NNU-35 after photocatalysis reaction.

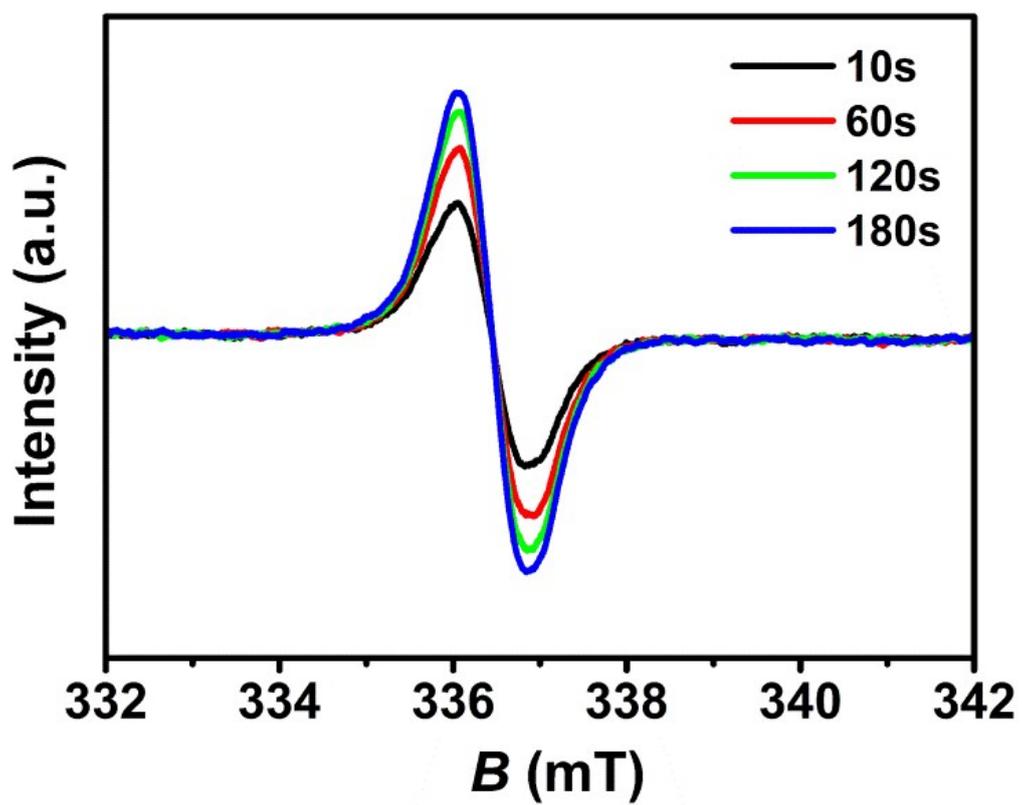


Fig. S4 In situ time-evolution EPR spectra of pillaring ligand L₁ in solid state under visible light .

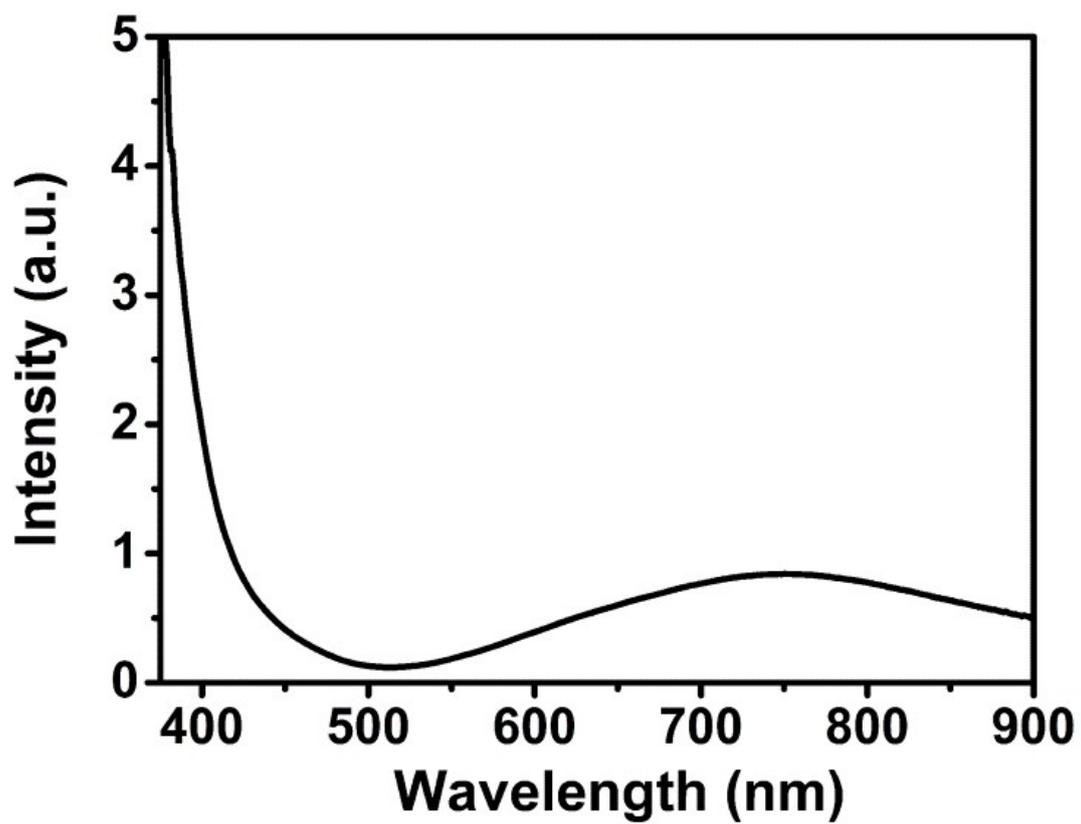


Fig. S5 UV-vis spectrum for the ATRP reaction without NNU-35.

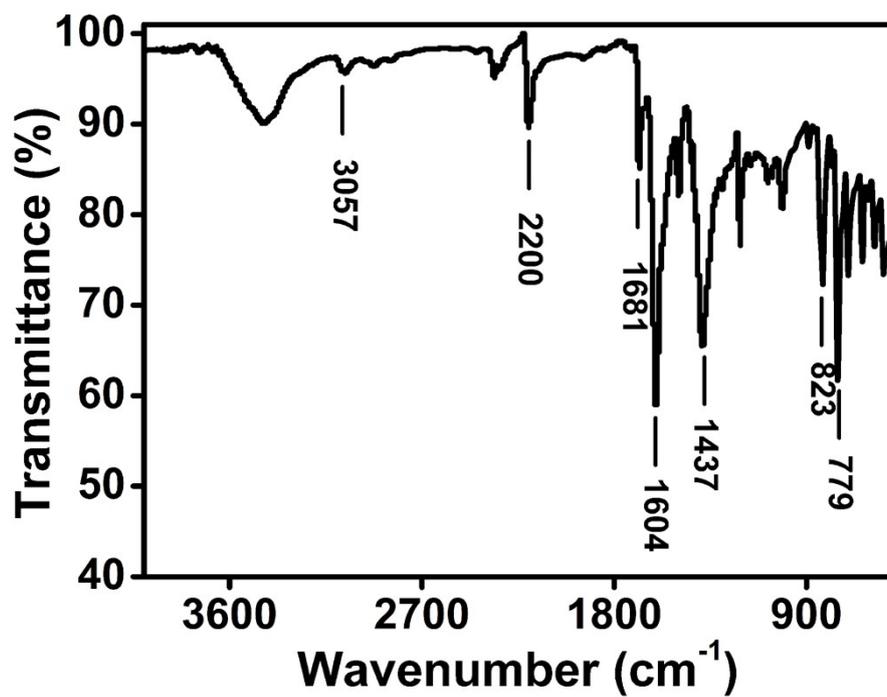


Fig. S6 IR spectrum of NNU-35.

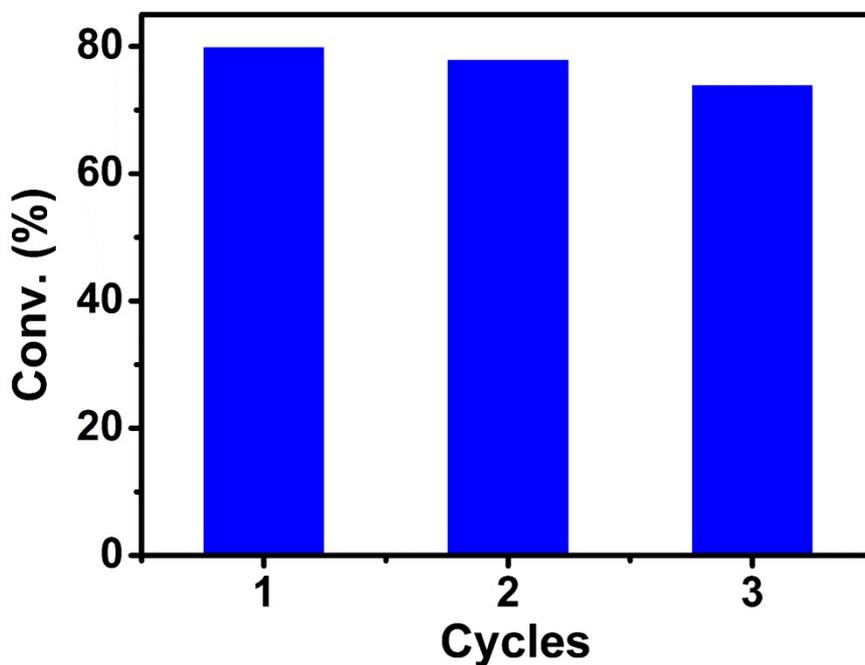


Fig. S7 The reuse of NNU-35 to initiate the visible-light-induced polymerization of MMA. $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PMDETA]_0 = 200/1/0.2/0.6$ in 2mL acetonitrile, NNU-35 = 20 mg, irradiation time = 14 h.

References:

- 1 T. M. Fasina, J. C. Collings, D. P. Lydon, D. Albesa-Jove, A. S. Batsanov, J.A. K. Howard, P. Nguyen, M. Bruce, A. J. Scott, W. Clegg, S. W. Watt, C. Viney, T. B. Marder, *J. Mater. Chem.* 2004, **14**, 2395-2404.
- 2 S. Winter, E. Weber, L. Eriksson, I. Csoregh, *New J. Chem.* 2006, **30**, 1808-1819.
- 3 G. M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.