4+4 Strategy for synthesis of zeolitic metal-organic frameworks: indium-MOF with SOD topology as light-harvesting antenna

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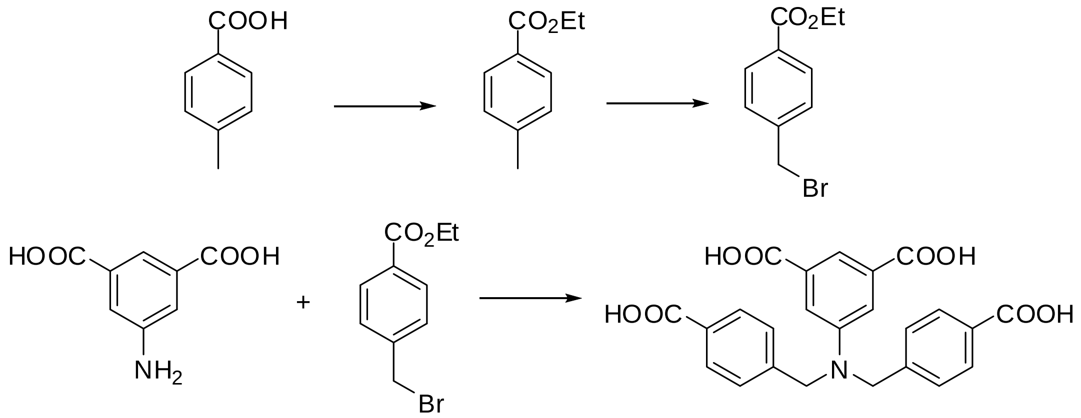
1. Experiments and Characterizations

1.1 Experimental section

1.1.1 Synthesis of 5-(bis(4-carboxybenzyl)amino)isophthalic acid (H_4BCBAIP)



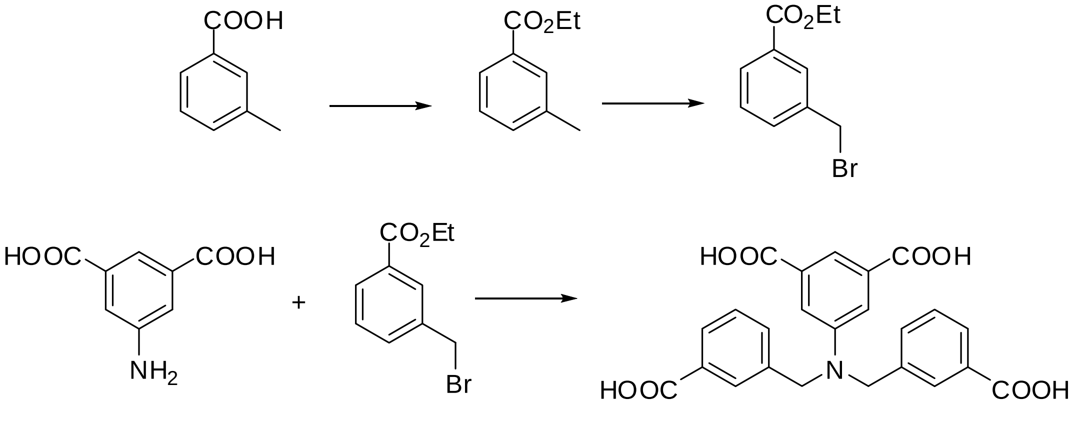
H_4BCBAIP

1.1.1.1 **Synthesis of ethyl 4-methylbenzoate.** The synthesis procedure of ethyl 4-methylbenzoate was similar to that reported in the literature[1]. Thionyl chloride (23.5 mL, 0.331 mol) was added dropwise at 0 °C to a stirred solution of 4-methylbenzoic acid (30.0 g, 0.221 mol) in absolute ethanol (200 mL). After stirring under reflux for 5 h, ethanol was evaporated under reduced pressure. The crude residue was dissolved in ethyl acetate, and washed with a saturated $NaHCO_3$ aqueous solution. After dried with anhydrous $MgSO_4$, ethyl acetate was evaporated under reduced pressure to afford 4-methylbenzoate as yellow oil. The product was directly used for the next experiment.

1.1.1.2 **Synthesis of ethyl 4-(bromomethyl)benzoate.** The synthesis of ethyl 4-(bromomethyl)benzoate was according to the literature.[2] Into a 250 mL round-bottom flask were added ethyl 4-methylbenzoate (20.944 g, 0.128 mol), NBS (23.73 g, 0.134 mol) and catalytic amount of benzoyl peroxide (3.035 g, 0.013 mol) with 150 mL of carbon tetrachloride. The solution was refluxed overnight. After cooled to room temperature, the solution was filtered and the filtrate was concentrated under reduced pressure to afford 4-(bromomethyl)benzoate as yellow oil. The product was directly used for the next experiment.

1.1.1.3 **Synthesis of H_4BCBAIP.** To the solution of ethyl 4-(bromomethyl)benzoate (21.351 g, 0.088 mol) in 175 mL H_2O was added dropwise KOH (13.141g, 0.235 mol) dissolved in 175 mL H_2O in a 3-necked flask. After being stirred for about 30 min, 5-aminoisophthalic acid (5.303 g, 0.029 mol) was added in small portions to the system. The resulting solution was kept at 80 °C with stirring for about 30 h. The mixture was cooled to room temperature and acidified with HCl aq (2M) and then filtered. Recrystallization from THF gave the product as white powder. ^{1}H NMR (300 M, DMSO-*d6*) $\delta = 7.91$ (d, $J = 8.4$ HZ, 4H), 7.76 (s, 1H), 7.37 (d, $J = 8.1$ Hz, 4H), 7.36 (s, 2H), 4.87 (s, 4H). ^{13}C NMR (75 MHz, DMSO-*d6*) δ = 167.1, 167.0, 148.1, 143.4, 132.1, 128.7, 126.6, 118.1, 116.5, 54.4.

1.1.2 Synthesis of 5-(bis(3-carboxybenzyl)amino)isophthalic acid (H_4BCBAIP')



H_4BCBAIP'

1.1.2.1 **Synthesis of ethyl 3-methylbenzoate.** The synthesis is similar to that of ethyl 4-methylbenzoate, except that the 4-methylbenzoic acid (30.0 g, 0.221 mol) is changed to 3-methylbenzoic acid (30.0 g, 0.221 mol).

1.1.2.2 **Synthesis of ethyl 3-(bromomethyl)benzoate.** The synthesis was similar to that of ethyl 4-(bromomethyl)benzoate, except that the ethyl 4-methylbenzoate (20.944 g, 0.128 mol) was changed to 3-methylbenzoate (20.944 g, 0.128 mol).

1.1.2.3 **Synthesis of H_4BCBAIP'.** The synthesis was similar to that of **H_4BCBAIP**, except that the ethyl 4-(bromomethyl)benzoate (21.351 g, 0.088 mol) was changed to 3-(bromomethyl)benzoate (21.351 g, 0.088 mol).

1.1.3 Synthesis of compound 1

$H_4BCBAIP$ (40 mg, 0.089 mmol) and $InCl_3{\cdot}4H_2O$ (45 mg,0.157 mmol) were added to a solution of DEF (2 mL) and C_2H_5OH (0.5 mL) and stirred for about 10 min, then the mixture was sealed in a 20 mL vial and heated at 95 ^{o}C for 3 days. The samples were cooled to room temperature, washed with C_2H_5OH and air-dried. The brown block crystals were obtained.

1.1.4 The Dye adsorption experiment

Several batches of sample **1** (25 mg) were added to the methanol solution (2 mL) containing 0.05 mg of different dyes including Methylene Blue (MB), Rhodamine B (RB), Rhodamine 6G (R6G), Coumarin 343 (C343) and Coumarin 6 (C6), respectively. The liquid state UV-vis adsorption spectra were taken every fixed mininutes over a period of 6 h. The products obtained were named **MB@1**, **RB@1**, **R6G@1**, **C343@1** and **C6@1**, respectively

1.1.5 The light-harvesting experiment

Samples of **1** (25 mg) were added to the methanol solution (2 mL) containing different amount of dyes including Coumarin 6 and Coumarin 343, respectively. After 24 h, the samples were filtered and washed with small amount of methanol for several times and air-dried. The solid state UV-vis absorption spectra were taken. The content of dyes was evaluated by a standard curve method.

1.2 Physical Characterizations

Infrared spectra were recorded on a Nicolet Impact 410 FTIR spectrometer in the range of 400-4000 cm^{-1}. Thermogravimetric analyses (TGA) were carried out with the Perkin-Elmer TGA-7 thermogravimetric analyzer. The samples were heated with 10 K/min to 800 ^{o}C in air. ^{1}H and ^{13}C NMR spectra were obtained with a Varian Mercuryvx 300 spectrometer. Surface areas and pore size distributions were measured by N_2 adsorption isotherms at 77 K with a Micrometrics ASAP 2020 instrument. The CO_2 sorption was measured at 273 K. The samples were exchanged with MeOH and evacuated at 85 ^{o}C for 10 h before each measurement. The framework of this as-synthesized compound **1** appears flexible due to the semi-flexible ligand. The XRD pattern of **1** activated at 85 ^{o}C with removal of the occluded guest solvents reveals that the reflection peaks shift to higher angles (Fig. S9b, ESI). This phenomenon was also observed in other works.[3] Photoluminescent spectra were measured on a RF-5301 PC spectrometer. The solid state UV-vis absorption spectra were taken on a HITACHI U-4100 spectrophotometer while the liquid spectra were taken on a SHIMADZU UV-2450 UV-visible spectrophotometer. The fluorescence decay spectra were obtained on a FLS920 with laser source of 405 nm.

1.3 X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Apex II CCD diffractometer for compound **1**, with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at 296 K. Data processing was accomplished with the SAINT processing program.[4] The structure of **1** was solved by the direct method and refined on F^2 by full-matrix least-squares with the SHELEX-97 program.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed geometrically. Attempts to locate and model the highly disordered solvent molecules in the pores were unsuccessful. Therefore, the SQUEEZE routine of PLATON was used to remove the diffraction contribution from guests to produce a set of solvent-free diffraction intensities.[6] The formula was designated from the electrons resulted after the SQUEEZE routine and the experimental results (see CIF†). The summary of the crystallographic data and refinement parameters is given in Table S2. The selected bond lengths and angles of **1** are given in Table S3.

References:

1. I. Aujard, J.-P. Baltaze, J.-B. Baudin, E. Cogné, F. Ferrage, L. Jullien, É. Perez, V. Prévost, L. M. Qian and O. Ruel, *J. Am. Chem. Soc.*, 2001, **123**, 8177.
2. A. Orita, H. Taniguchi and J. Otera, *Chem. Asian J.*, 2006, **1**, 430.
3. (a) L. Du, Z. Lu, K. Zheng, J. Wang, X. Zheng, Y. Pan, X. You and J. Bai, *J. Am. Chem. Soc.*, 2013, **135**, 562; (b) A.-X. Zhu, J.-B. Lin, J.-P. Zhang and X.-M. Chen, *Inorg. Chem.*, 2009, **48**, 3882; (c) Y.-S. Wei, K.-J. Chen, P.-Q. Liao, B.-Y. Zhu, R.-B. Lin, H.-L. Zhou, B.-Y. Wang, W. Xue, J.-P. Zhang and X.-M. Chen, *Chem.*

Sci., 2013, **4**, 1539; (d) B. Zheng, Z. Yang, J. Bai, Y. Li and S. Li, *Chem. Commun.*, 2012, **48**, 7025; (e) E. Jeong, W. R. Lee, D. W. Ryu, Y. Kim, W. J. Phang, E. K. Koh and C. S. Hong, *Chem. Commun.*, 2013, **49**, 2329; (f) D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem. Int. Ed.*, 2004, **43**, 5033.

4. E. C. P. Bruker AXS Inc., Madison, WI 53711-5373, USA, 2000.
5. G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 2008, **64**, 112.
6. (a) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7; (b) A.L.Spek, *Acta Crystallogr.*, *Sect. D*, 2009, **65**, 148.

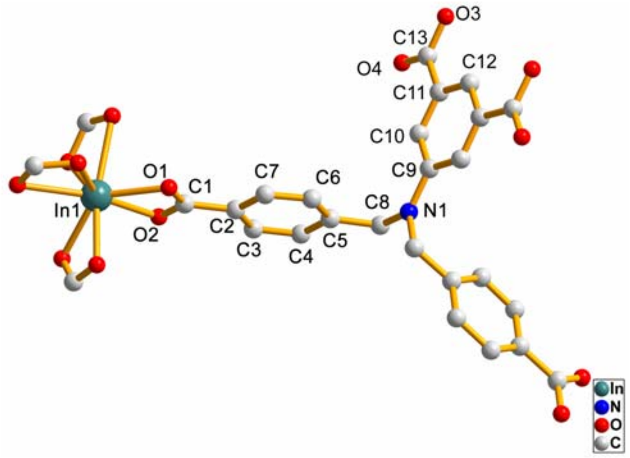


Fig. S1 The coordination environment of **1**. The atoms labeled represent the asymmetric unit.

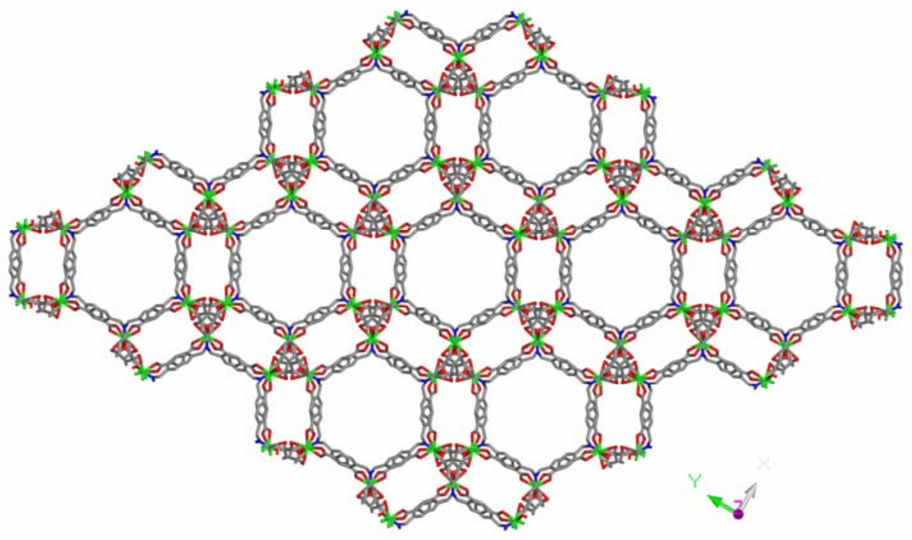


Fig. S2 The 3D structure viewed along the [001] direction.

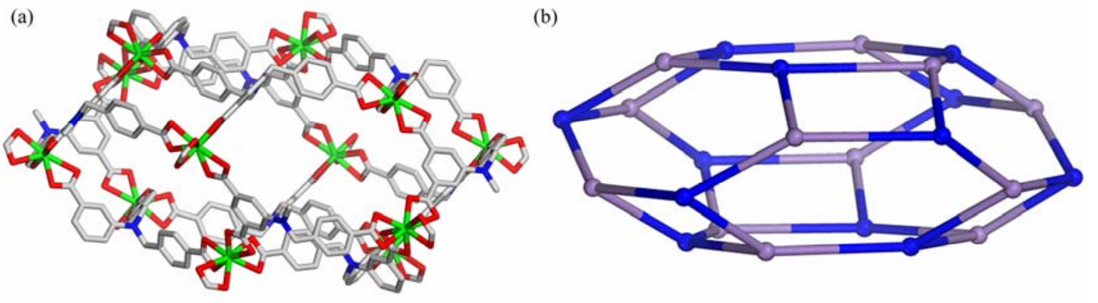


Fig. S3 The distorted sodalite cage in the framework (a) and the topological structure (b).

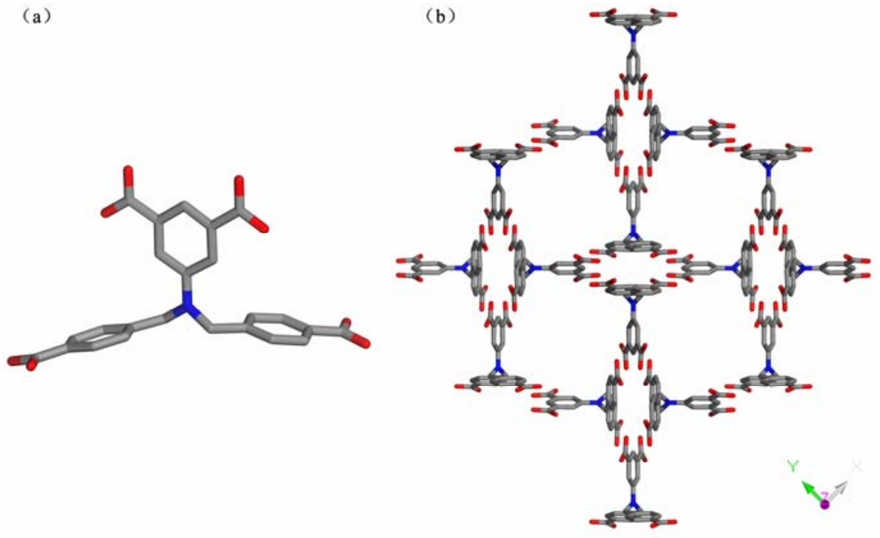


Fig. S4 Structure of pure H$_4$BCBAIP. (a) The tetrahedral configuration of **H$_4$BCBAIP**; (b) the 2D layer viewed along the [001] direction.

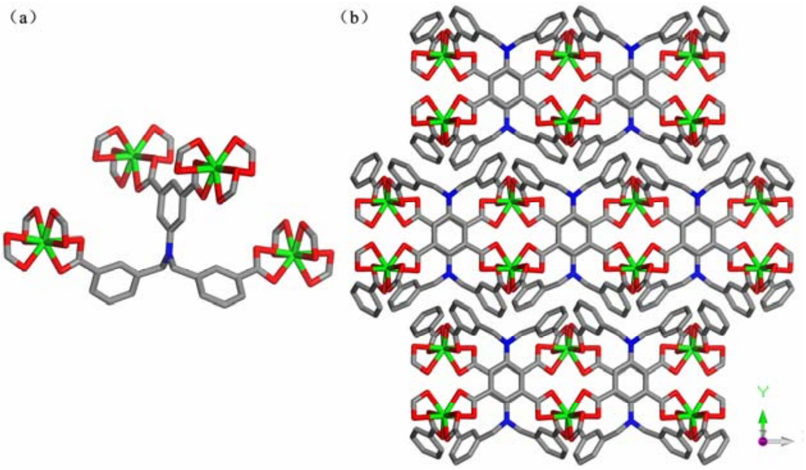


Fig. S5 Structure of 2D In-MOF. (a) The 4-connected BCBAIP'$^{4-}$; (b) the 2D layer viewed along the [001] direction.

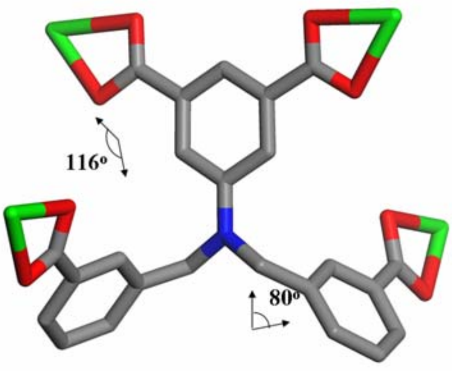


Fig. S6 The T-L-T angles of BCBAIP'$^{4-}$.

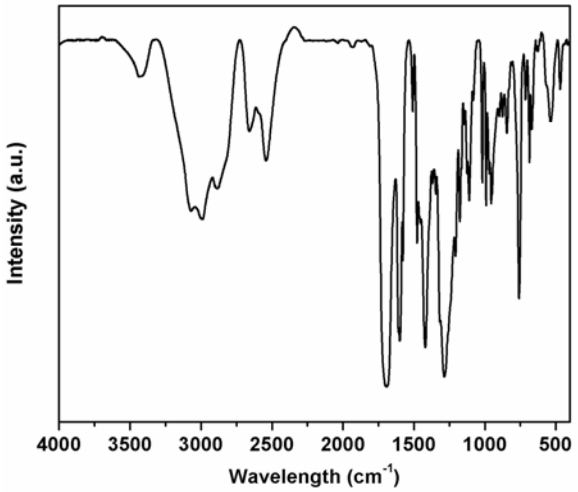


Fig. S7 The FT-IR spectrum of **1**.

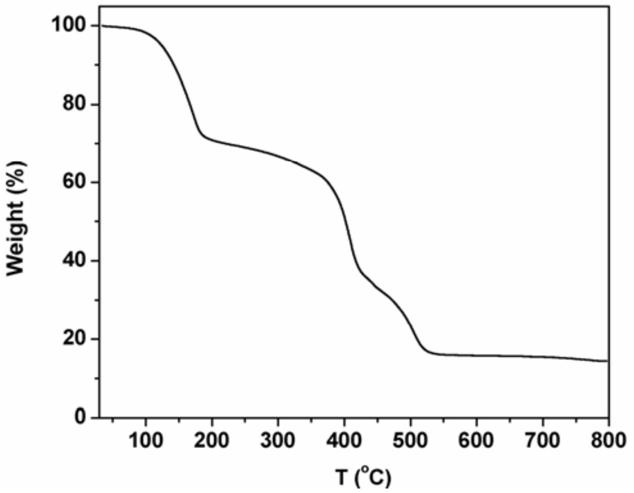


Fig. S8 The TGA curve of **1**.

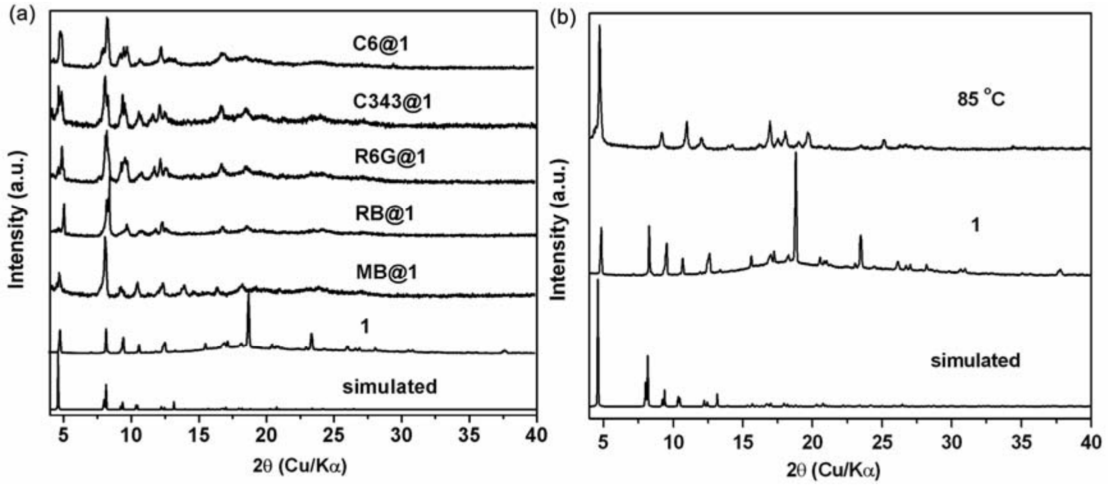


Fig. S9 (a) Powder X-ray diffraction patterns of the dyes loaded samples. (b) Powder X-ray diffraction patterns of as-synthesized **1** and the activated samples at 85 °C.

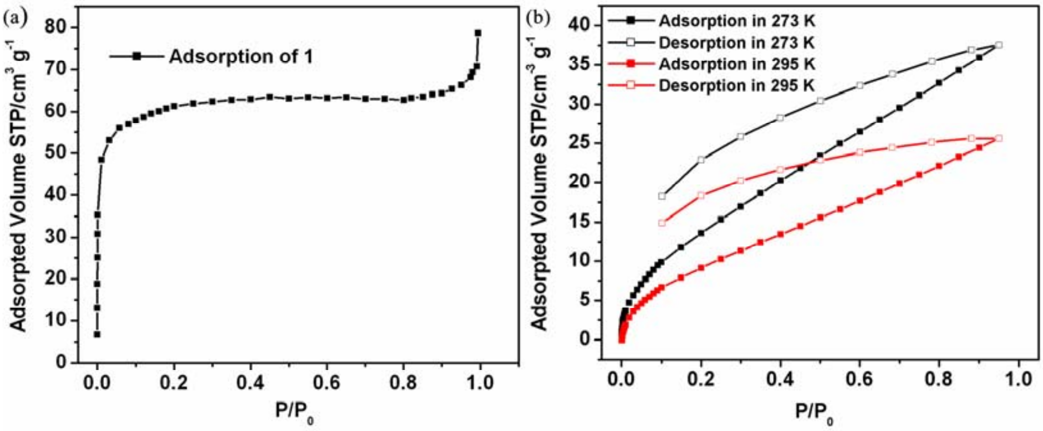


Fig. S10 (a) N_2 adsorption isotherm at 77 K. (b) CO_2 adsorption-desorption isotherms at 273 and 295 K.

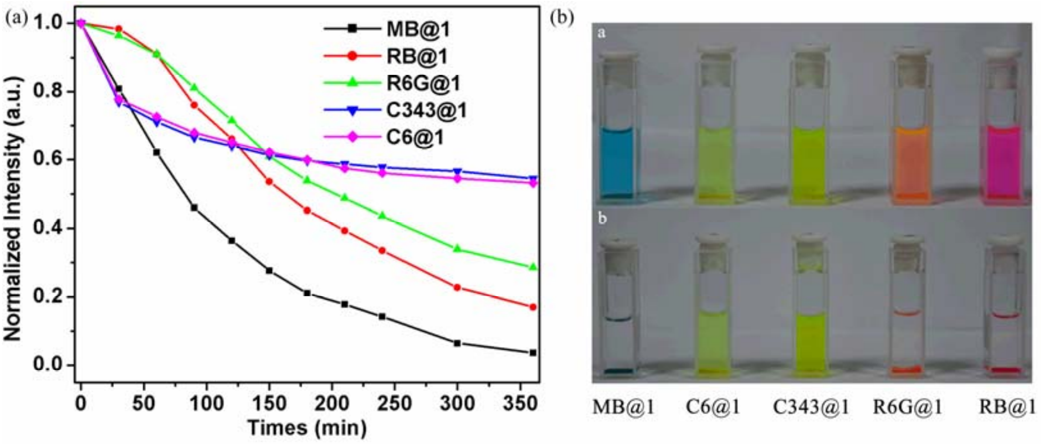


Fig. S11 (a) The kinetic absorption curves for **dyes@1**. (b) The photos before and after the adsorption experiments under sunlight.

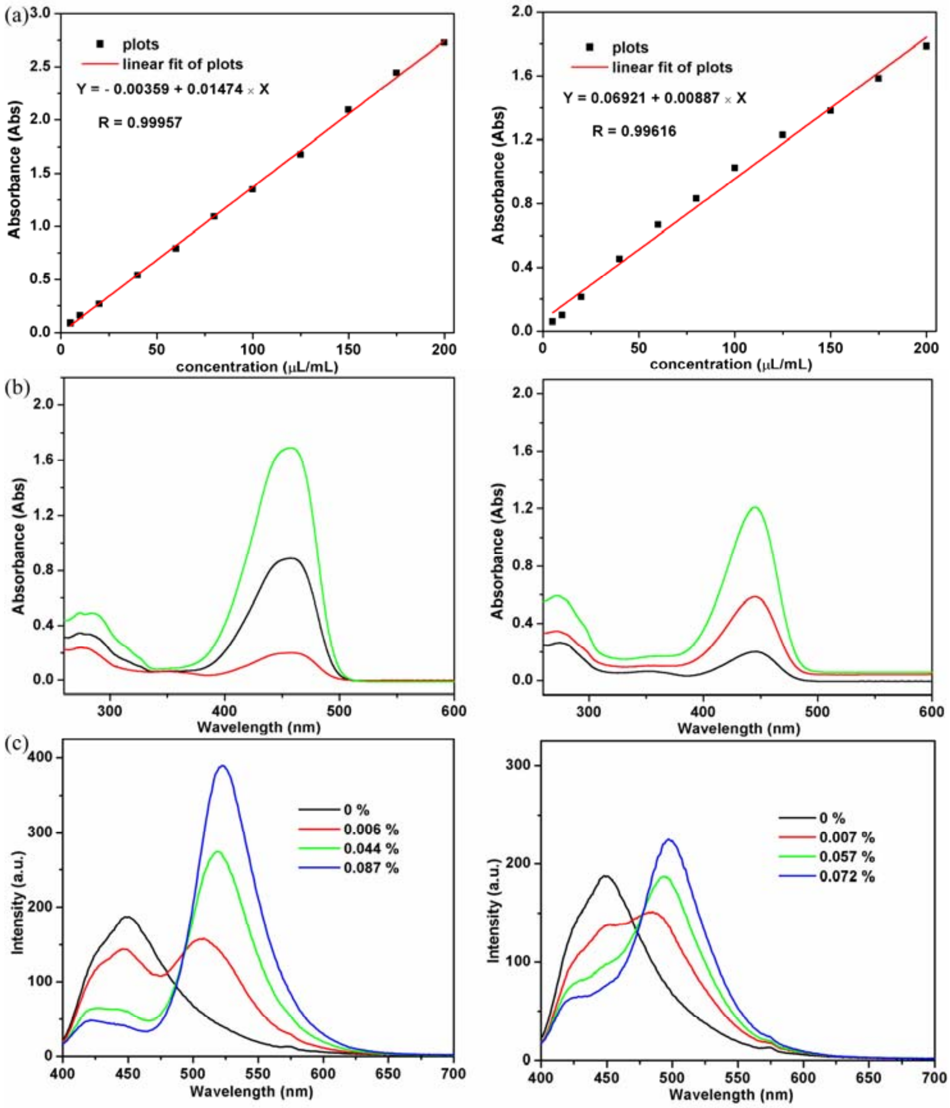


Fig. S12 (a) The standard curves of the UV-vis absorption. (b) The dyes remained in the methanol after the adsorption with **1**. (c) The light-harvesting process (left: C6, right: C343).

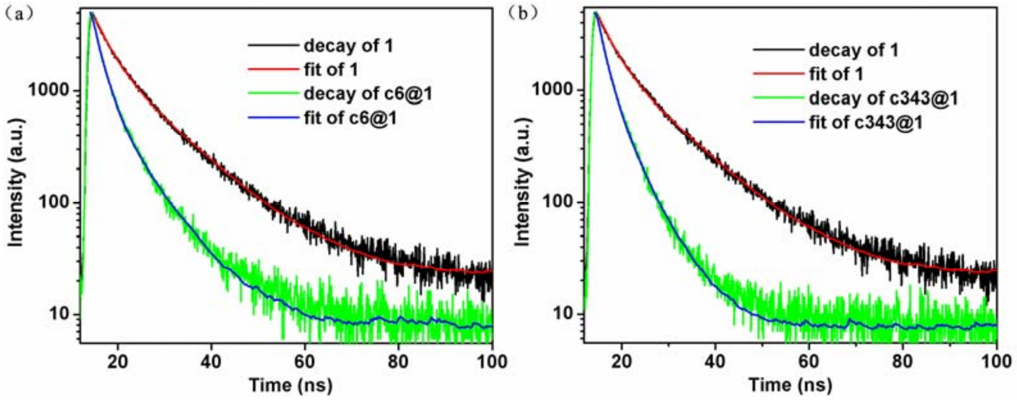


Fig. S13 Fluorescence decay profiles (Ex: 405 nm) of **1**, **C6@1**, C**343@1** monitored at 450 nm. The lifetimes are listed on Table S1.

Table S1 Lifetimes of **1**, **C6@1**, **C343@1**.

compound	τ (ns)
1	2.76
C6@1	1.87
C343@1	1.72

Table S2 Crystallographic data for **1**

Empirical formula	$C_{56}H_{95}N_6O_{16}In$
Formula weight	1223.20
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, *R*-3*c*
Unit cell dimensions	a = 38.2369(10) Å α = 90° b = 38.2369(10) Å β = 90° c = 22.7356(12) Å γ = 120°
Volume	28787.4(19) $Å^3$
Z	18
Calculated density	1.270 g cm^{-3}
Absorption coefficient	0.436 mm^{-1}
F(000)	11700
Theta range for data collection	1.07 to 28.29 °
Limiting indices	$-32 \le h \le 50$, $-50 \le k \le 48$, $-30 \le l \le 30$
Reflections collected / unique	69588 / 7969
R_{int}	0.0947
Completeness to theta = 2748	100.0 %
Absorption correction	Semi-empirical from equivalents
Max and min transmission	0.7457 and 0.5683
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7969 / 0 / 156
Goodness-of-fit on F^2	1.009
Final *R* indices[a] [I>2$\sigma(I)$]	R_1 = 0.0448, wR_2 = 0.0788
R indices (all data)	R_1 = 0.1513, wR_2 = 0.0878
Largest diff peak and hole	0.574 and -0.208 e $Å^{-3}$

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(0.0231P)^2+000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table S3 Bond lengths [Å] and angles [°] for **1**

In(1)-O(1)	2.268(2)	In(1)-O(1)#3	2.268(2)
In(1)-O(2)	2.2721(19)	In(1)-O(2)#3	2.2720(19)
In(1)-O(3)#1	2.187(2)	In(1)-O(3)#2	2.187(2)
In(1)-O(4)#1	2.473(2)	In(1)-O(4)#2	2.473(2)
N(1)-C(8)#4	1.473(3)	N(1)-C(8)	1.473(3)
N(1)-C(9)	1.404(5)	O(1)-C(1)	1.217(4)
O(2)-C(1)	1.282(3)	O(3)-C(13)	1.280(3)
O(3)-In(1)#2	2.187(2)	O(4)-C(13)	1.223(3)
O(4)-In(1)#2	2.473(2)	C(1)-C(2)	1.510(4)
C(2)-C(7)	1.369(4)	C(2)-C(3)	1.371(4)
C(3)-C(4)	1.399(4)	C(4)-C(5)	1.367(4)
C(5)-C(6)	1.364(4)	C(5)-C(8)	1.485(3)
C(6)-C(7)	1.378(3)	C(9)-C(10)	1.385(3)
C(9)-C(10)#4	1.385(3)	C(10)-C(11)	1.352(3)
C(11)-C(12)	1.363(3)	C(11)-C(13)	1.488(4)
C(12)-C(11)#4	1.363(3)	C(13)-In(1)#2	2.699(4)

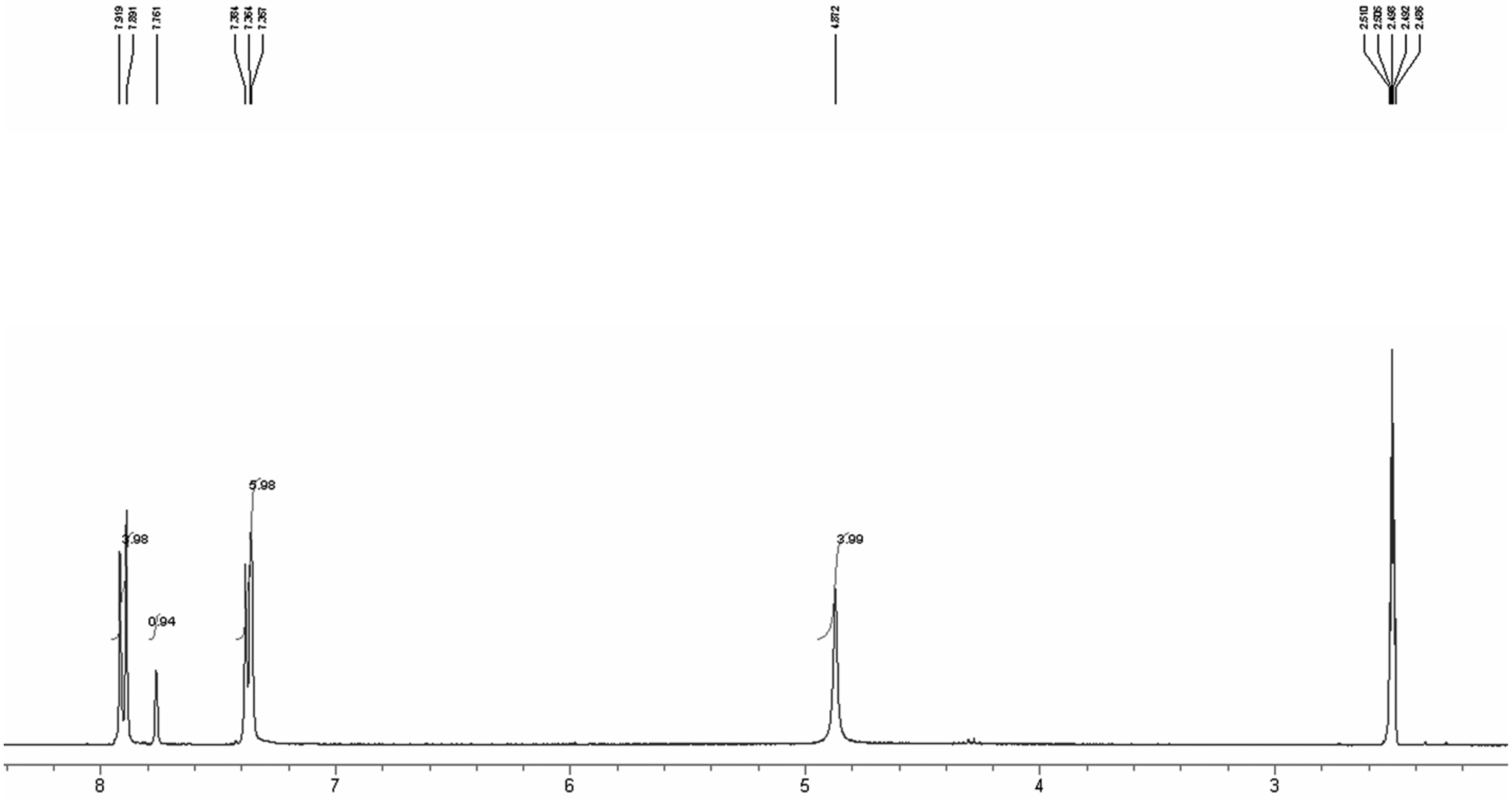
O(1)#3-In(1)-O(1)	129.11(11)	O(1)#3-In(1)-O(2)#3	57.47(7)
O(1)-In(1)-O(2)#3	86.02(8)	O(1)#3-In(1)-O(2)	86.02(8)
O(1)-In(1)-O(2)	57.47(7)	O(1)#3-In(1)-O(4)#1	79.64(8)
O(1)-In(1)-O(4)#1	137.96(8)	O(1)#3-In(1)-O(4)#2	137.96(8)
O(1)-In(1)-O(4)#2	79.64(8)	O(1)#3-In(1)-C(1)#3	27.92(8)
O(1)-In(1)-C(1)#3	109.28(10)	O(1)#3-In(1)-C(1)	109.28(10)
O(1)-In(1)-C(1)	27.92(8)	O(1)#3-In(1)-C(13)#2	111.33(11)
O(1)-In(1)-C(13)#2	102.78(10)	O(1)#3-In(1)-C(13)#1	102.78(10)
O(1)-In(1)-C(13)#1	111.33(11)	O(1)-C(1)-O(2)	121.7(3)
O(1)-C(1)-C(2)	122.1(3)	O(1)-C(1)-In(1)	60.76(18)
O(2)#3-In(1)-O(2)	90.09(10)	O(2)#3-In(1)-O(4)#1	87.92(7)
O(2)-In(1)-O(4)#1	164.13(8)	O(2)#3-In(1)-O(4)#2	164.12(8)
O(2)-In(1)-O(4)#2	87.92(7)	O(2)#3-In(1)-C(1)#3	29.55(9)
O(2)-In(1)-C(1)#3	87.69(8)	O(2)#3-In(1)-C(1)	87.69(8)
O(2)-In(1)-C(1)	29.55(9)	O(2)#3-In(1)-C(13)#2	168.81(10)
O(2)-In(1)-C(13)#2	88.92(8)	O(2)#3-In(1)-C(13)#1	88.92(8)
O(2)-In(1)-C(13)#1	168.80(10)	O(2)-C(1)-C(2)	116.2(4)
O(2)-C(1)-In(1)	60.96(16)	O(3)#1-In(1)-O(3)#2	114.40(12)
O(3)#1-In(1)-O(1)#3	125.34(8)	O(3)#2-In(1)-O(1)#3	83.52(9)
O(3)#1-In(1)-O(1)	83.52(9)	O(3)#2-In(1)-O(1)	125.33(8)
O(3)#1-In(1)-O(2)#3	89.38(8)	O(3)#2-In(1)-O(2)#3	140.92(9)
O(3)#1-In(1)-O(2)	140.92(9)	O(3)#2-In(1)-O(2)	89.38(8)
O(3)#1-In(1)-O(4)#1	54.83(7)	O(3)#2-In(1)-O(4)#1	82.32(7)
O(3)#1-In(1)-O(4)#2	82.32(7)	O(3)#2-In(1)-O(4)#2	54.83(7)
O(3)#1-In(1)-C(1)#3	109.43(10)	O(3)#2-In(1)-C(1)#3	111.41(11)
O(3)#1-In(1)-C(1)	111.41(11)	O(3)#2-In(1)-C(1)	109.43(10)

O(3)#1-In(1)-C(13)#2	98.39(9)	O(3)#2-In(1)-C(13)#2	27.93(8)
O(3)#1-In(1)-C(13)#1	27.93(8)	O(3)#2-In(1)-C(13)#1	98.39(9)
O(3)-C(13)-C(11)	117.5(3)	O(3)-C(13)-In(1)#2	53.17(18)
O(4)#1-In(1)-O(4)#2	98.16(11)	O(4)#1-In(1)-C(1)#3	82.83(9)
O(4)#2-In(1)-C(1)#3	165.61(11)	O(4)#1-In(1)-C(1)	165.61(11)
O(4)#2-In(1)-C(1)	82.83(9)	O(4)#1-In(1)-C(13)#2	89.99(7)
O(4)#2-In(1)-C(13)#2	26.91(7)	O(4)#1-In(1)-C(13)#1	26.91(7)
O(4)#2-In(1)-C(13)#1	89.99(7)	O(4)-C(13)-O(3)	119.3(4)
O(4)-C(13)-C(11)	123.1(3)	O(4)-C(13)-In(1)#2	66.2(2)
N(1)-C(8)-C(5)	114.7(2)	C(1)#3-In(1)-C(1)	99.81(13)
C(1)#3-In(1)-C(13)#2	139.25(13)	C(1)-In(1)-C(13)#2	96.86(9)
C(1)#3-In(1)-C(13)#1	96.86(10)	C(1)-In(1)-C(13)#1	139.25(13)
C(1)-O(1)-In(1)	91.3(2)	C(1)-O(2)-In(1)	89.5(2)
C(2)-C(1)-In(1)	177.2(3)	C(2)-C(3)-C(4)	120.1(3)
C(2)-C(7)-C(6)	120.5(3)	C(3)-C(2)-C(1)	122.3(3)
C(4)-C(5)-C(8)	118.7(3)	C(5)-C(6)-C(7)	122.0(3)
C(5)-C(4)-C(3)	121.3(3)	C(6)-C(5)-C(4)	117.6(3)
C(6)-C(5)-C(8)	123.7(3)	C(7)-C(2)-C(3)	118.5(3)
C(7)-C(2)-C(1)	119.1(3)	C(8)-N(1)-C(8)#4	114.6(3)
C(9)-N(1)-C(8)	122.72(17)	C(9)-N(1)-C(8)#4	122.72(17)
C(10)-C(11)-C(12)	120.7(3)	C(10)-C(11)-C(13)	118.9(3)
C(10)-C(9)-C(10)#4	116.8(4)	C(10)-C(9)-N(1)	121.6(2)
C(10)#4-C(9)-N(1)	121.6(2)	C(11)-C(13)-In(1)#2	170.5(3)
C(11)-C(12)-C(11)#4	119.0(4)	C(11)-C(10)-C(9)	121.4(3)
C(12)-C(11)-C(13)	120.4(3)	C(13)-O(3)-In(1)#2	98.9(2)
C(13)-O(4)-In(1)#2	86.9(2)	C(13)#2-In(1)-C(13)#1	94.19(12)

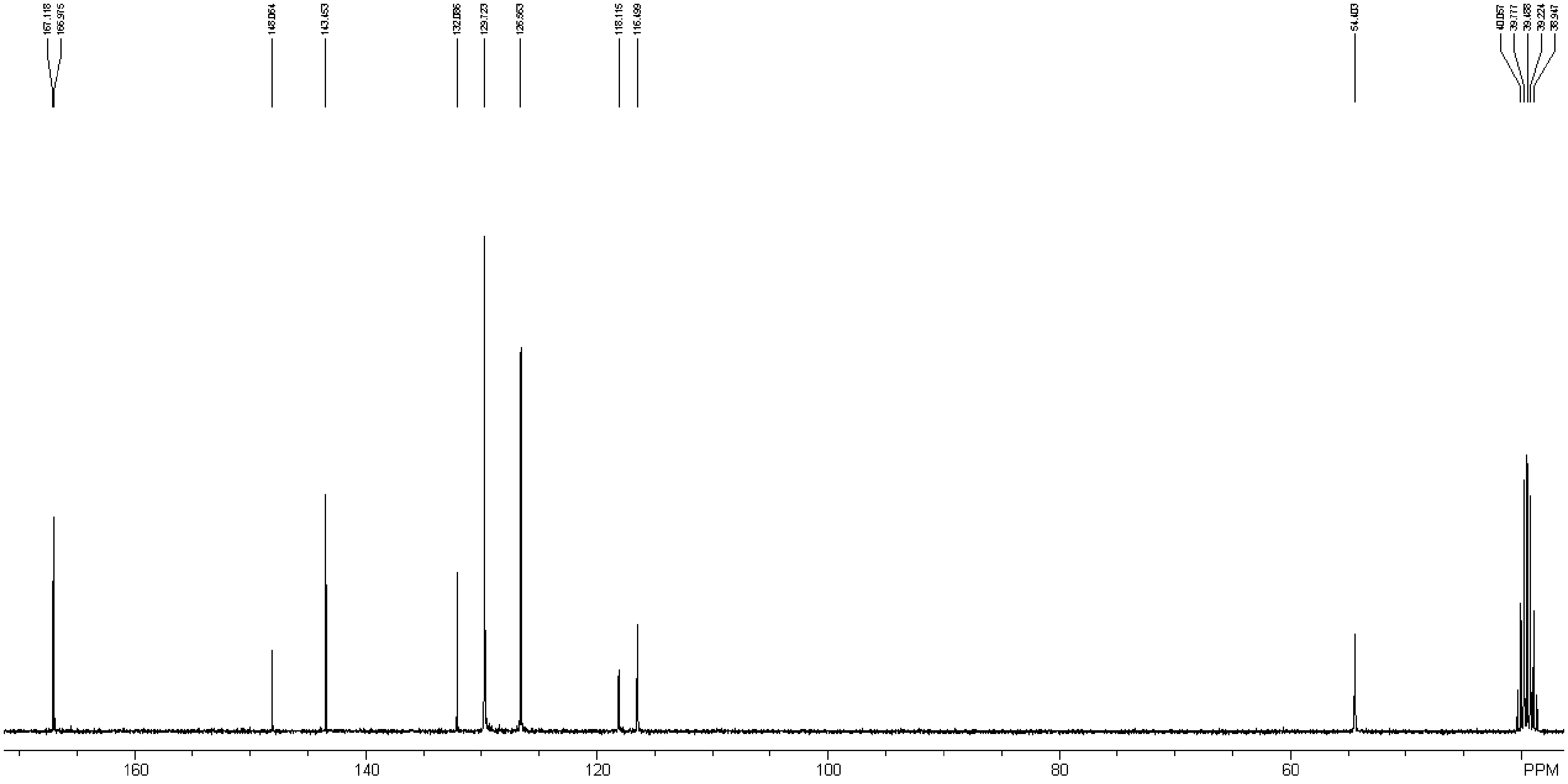
Symmetry transformations used to generate equivalent atoms:

#1 -y+1/3,-x+2/3,z+1/6 #2 -x+1,-y,-z

#3 y+1/3,x-1/3,-z+1/6 #4 -x+4/3,-x+y+2/3,-z+1/6



^{1}H NMR for H_4BCBAIP



^{13}C NMR for H_4BCBAIP