Supporting Information for

Supramolecular Self-Assembly of Chiral Helical Tubular Polymers with Amplified Circularly Polarized Luminescence

Xianhui Tang,[+] Dandan Chu,[+] Hong Jiang, Wei Gong, Chao Jiang, Yong Cui*, and Yan Liu*

Table of Content

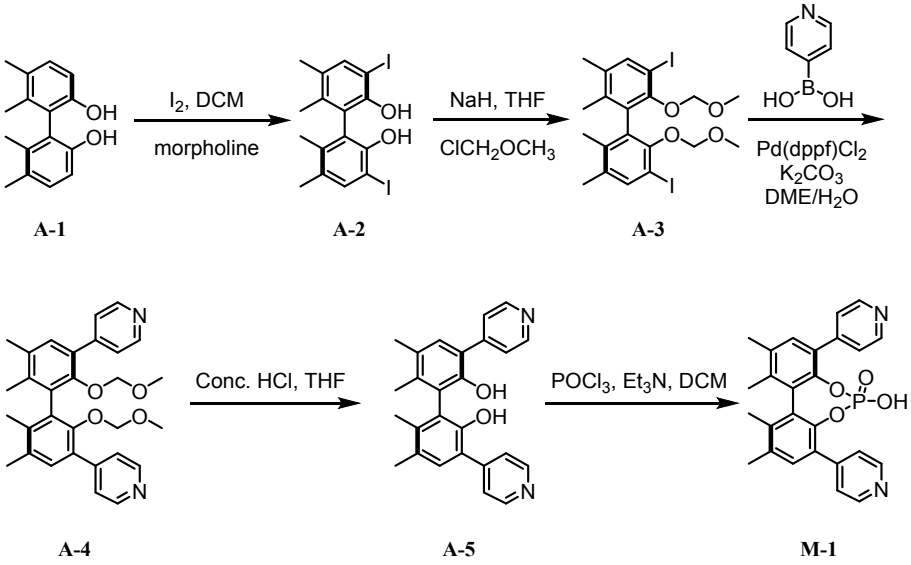
1. Materials and general procedures

All of the chemicals are commercial available, and used without further purification. Elemental analyses were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. The optical rotation were recorded on an Automatic polarimeter (PMS/JASCO P-2000). The CD spectra were recorded on a *J*-815 spectropolarimeter (Jasco, Japan). The circularly polarized luminescence (CPL) spectra were measured on a JASCO CPL-300 spectrophotometer. Excitation and emission spectra were recorded on the Steady-State & Time-Resolved Fluorescence Spectrofluorometer (QM/TM/IM). All the UV-vis absorption spectra were recorded on a Lambda 20 UV/Vis Spectrometer (Perkin Elmer, Inc., USA). Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 5 ^{o}C/min on a STA449C integration thermal analyzer. ^{1}H, ^{13}C and ^{31}P NMR experiments were carried out on a Bruker AVANCE III HD 400 spectrometer operating at resonance frequencies of 400 MHz.

X-ray Crystallography. Single-crystal XRD data for **1** and **2** were collected on BL17B beamline (λ = 0.71073 Å) of National Facility for Protein Science in Shanghai Synchrotron Radiation Facility (SSRF) at 173 K. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved by direct methods with SHELXS-2014 and refined by full-matrix least-squares on F^2 with SHELXL-2014[1] using *OLEX2-1.2*[2]. In the compound, all the non-hydrogen atoms except guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters, and the hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms, treated as riding atoms. The benzene ring atoms and pyridine ring atoms were geometrically restrained to fit idealized six membered, respectively. DFIX, SADI, FLAT, DANG and SIMU restrains were used to obtain reasonable parameters due to the poor quality of crystal data. The solvent molecules were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these highly disordered solvent molecules were removed using the SQUEEZE routine of PLATON[3]; Structures were then refined again using the data generated.

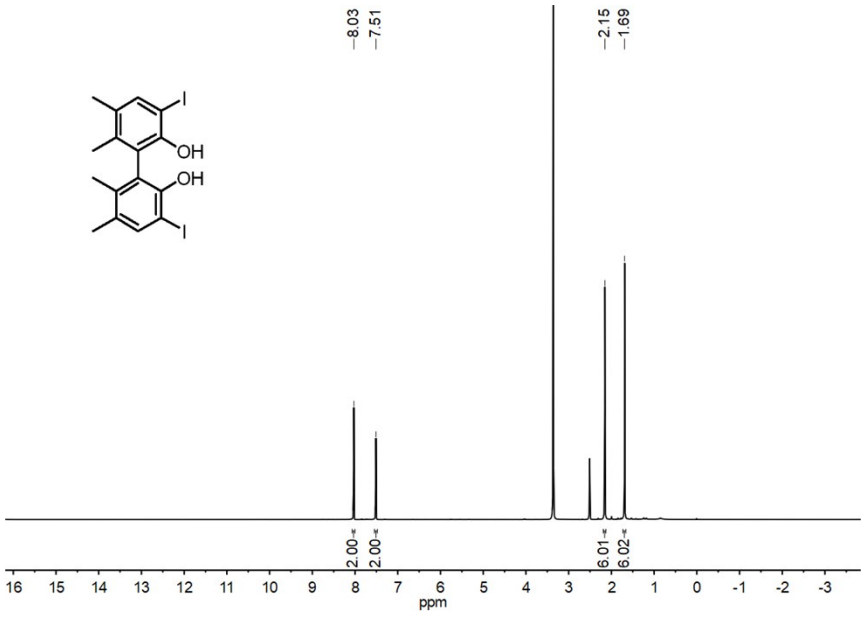
Crystal data and details of the data collection are given in **Table S1**, and selected bond distances and angles are presented in **Tables S2** and **S3**. CCDC 1999762 (**1**) and 1999763 (**2**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

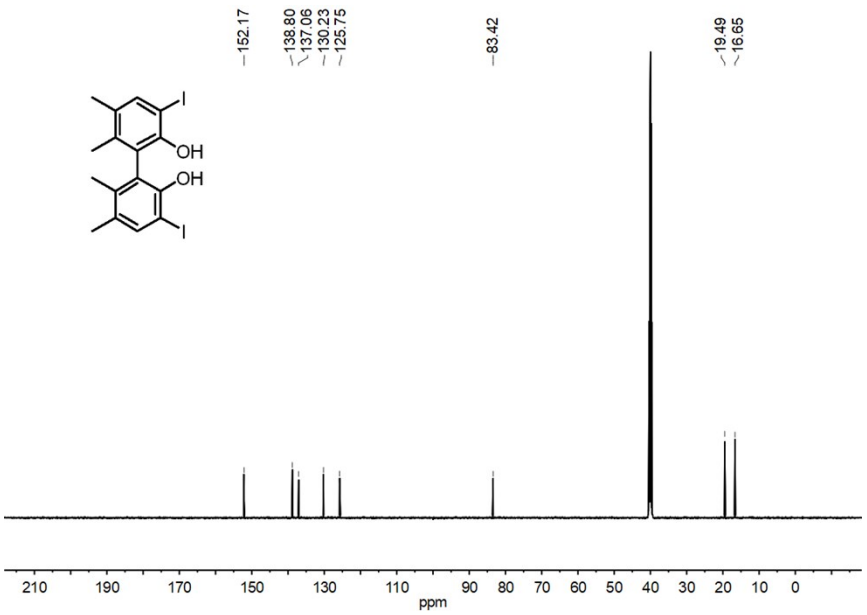
2. Synthesis



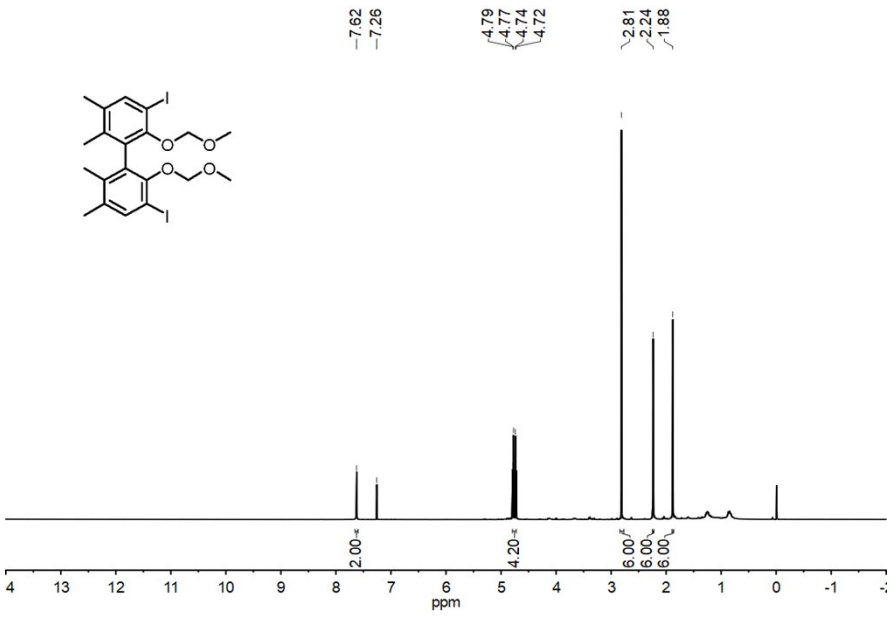
(*R*)-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol (**A-1**) was synthesized according to the published procedure.[4]

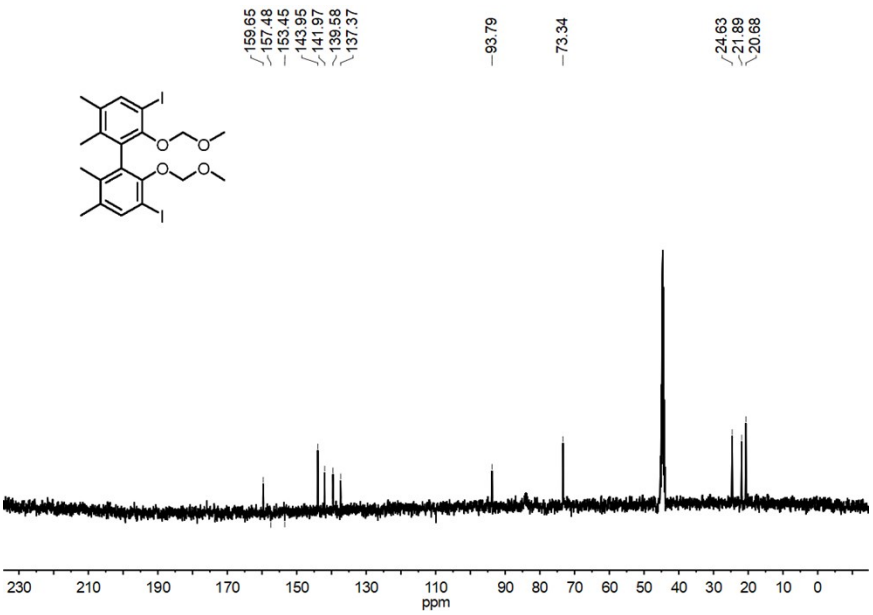
Synthesis of A-2. To a solution of **A-1** (12.11 g, 50 mmol) in CH_2Cl_2 (400 mL) was added successively morpholine (26.35 mL, 300 mmol) and I_2 (31.72 g, 125 mmol) at room temperature. The mixture was stirred for 10 h. After that, 2 M HCl (300 mL) was added. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with saturated $Na_2S_2O_3$ solution and brine, and then dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:10, v/v) to afford **A-2** ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.03 (s, 2H), 7.51 (s, 2H), 2.15 (s, 6H), 1.69 (s, 6H), ^{13}C NMR (DMSO-d_6, 126 MHz) δ: 152.17, 138.80, 137.06, 130.23, 125.75, 83.72, 19.49, 16.65.



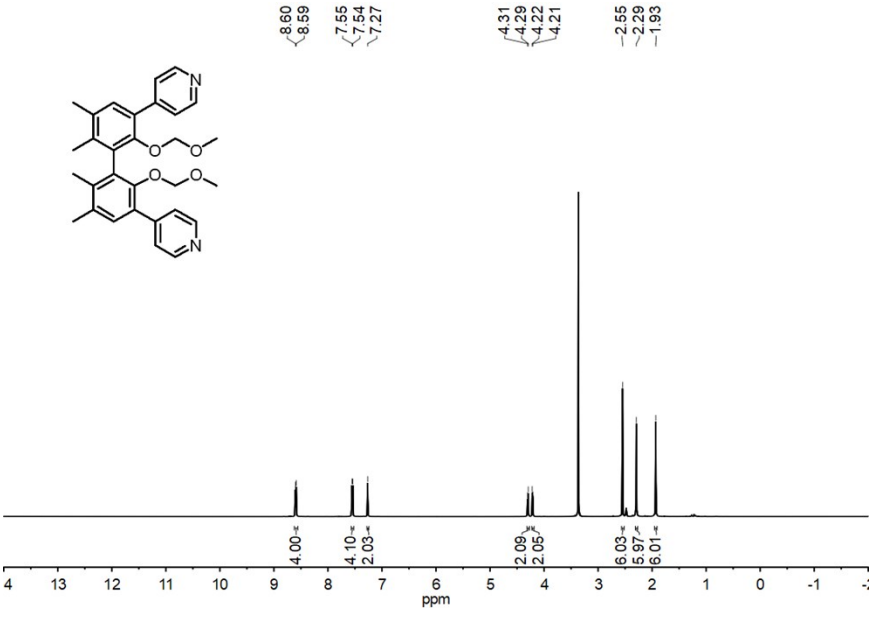


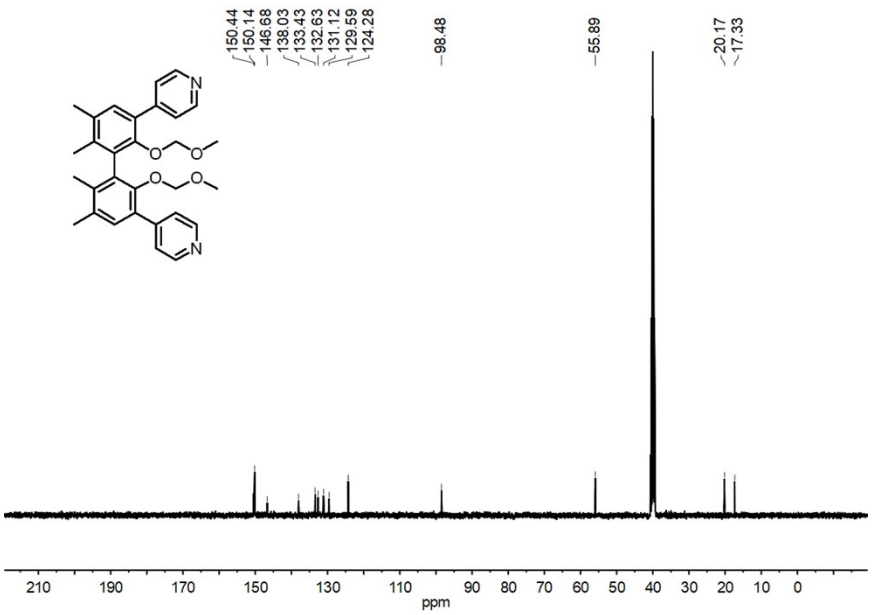
Synthesis of A-3 Under a nitrogen atmosphere, **A-2** (1.45 g, 4 mmol) in 10 mL DME was added dropwise to a stirred suspension of NaH (1.75 g, 43 mmol) in anhydrous DME (100 mL) at room temperature. The resulting mixture was stirred for 30 min, and then was heated to 55 °C and stirred at 55 °C for 1 h. After that, methoxymethyl chloride (13.60 mL, 48 mmol) was slowly added. The mixture was stirred for 2 h. Then the reaction was cooled to room temperature and quenched by water. The mixture was concentrated under reduced pressure and extracted with ethyl acetate. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent, the product **A-3** was obtained as a white solid (1.5 g, 81.7%), which was pure enough for the next step. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.62 (s, 2H), 4.75 (dd, J = 20 Hz, 8 Hz, 4H), 2.81 (s, 6H), 2.24 (s, 6H), 1.88 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) δ: 159.65, 143.95, 141.97, 139.58, 137.37, 93.79, 73.34, 24.63, 21.89, 20.68.



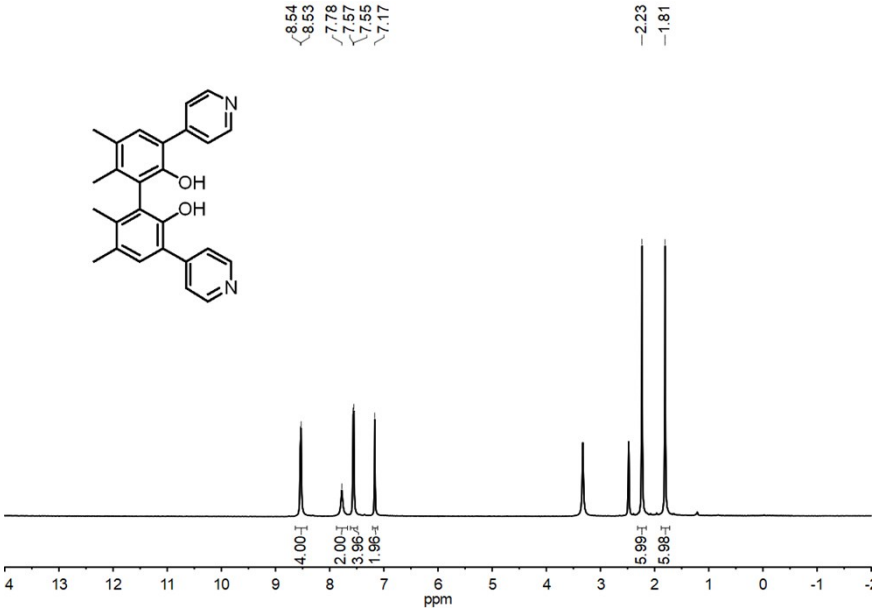


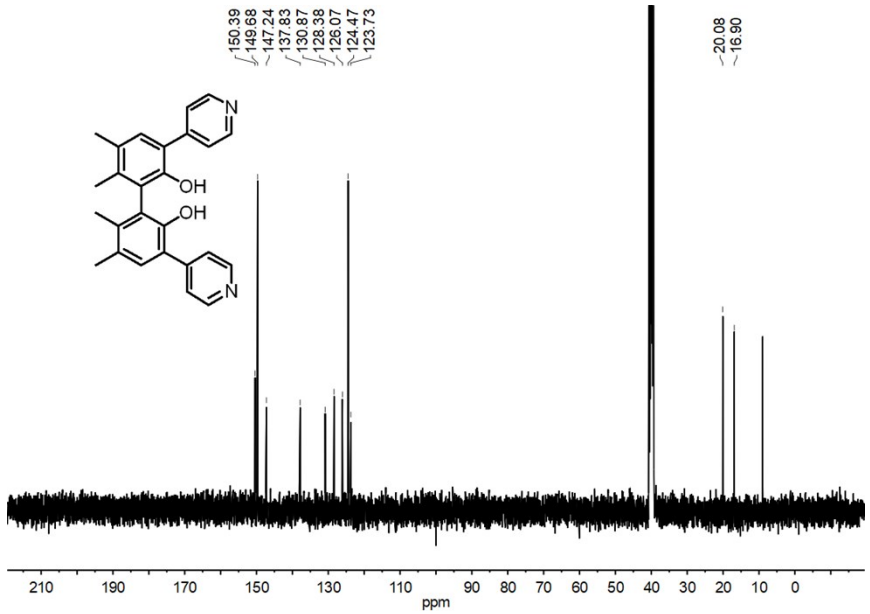
Synthesis of A-4. A-3 (4.94 g, 10 mmol), 4-pyridylboronic acid (3.69 g, 30 mmol), K_2CO_3 (8.28 g, 60 mmol) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.82 g, 1 mmol) were weighted into a two-neck 250 mL flask and the mixture was degassed for three times. DME (100 mL) and H_2O (50 mL) were added under a N_2 atmosphere. The mixture was stirred at 90 °C for 12 h. After cooling to room temperature, the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:1, v/v) to afford **A-4** as a white solid (3.52 g, 89%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.60 (d, J = 4 Hz, 4H), 7.55 (d, J = 4 Hz, 4H), 7.27 (s, 2H), 4.26 (dd, J = 36 Hz, 8 Hz, 4H), 2.55 (s, 6H), 2.29 (s, 6H), 1.93 (s, 6H); ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 150.44, 150.14, 146.68, 138.03, 133.43, 132.63, 131.12, 129.59, 124.28, 98.48, 55.89, 20.17, 17.33.



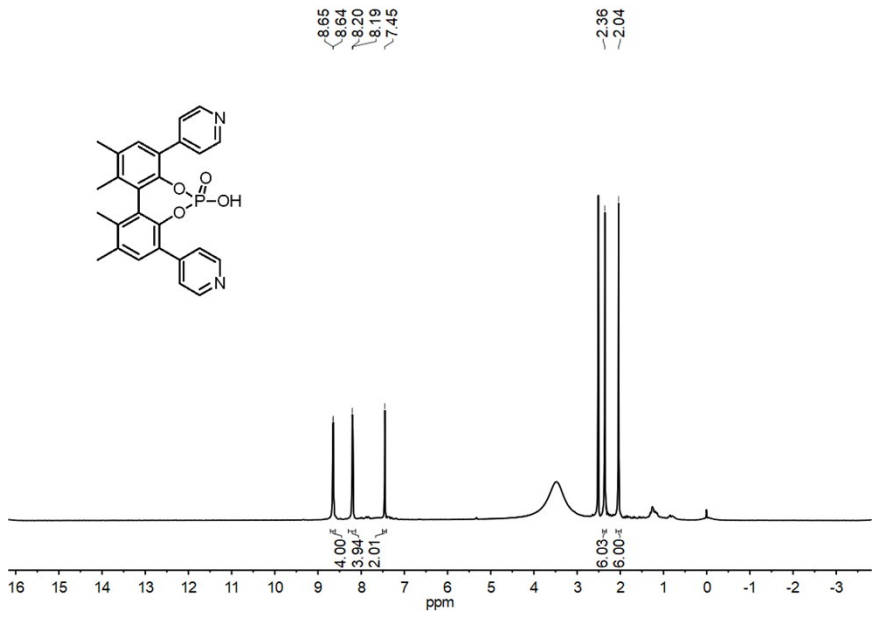


Synthesis of A-5. Concentrated HCl (6.50 mL, 6 M) was slowly added into a solution of **A-4** (1.20 g, 3.00 mmol) in 20 mL THF, and the mixture was then stirred at room temperature for 10 h. The mixture was concentrated under reduced pressure and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated. The crude product was purified by silica column (EtOAc/petroleum ether = 1/1) to give the compound **(*R*)-M-4** as white solid (1.16 g, 98%). ^{1}H NMR (DMSO-d_6, 400 M) δ: 8.54 (d, J = 4 Hz, 4H), 7.78 (br, 2H), 7.56 (d, J = 8 Hz, 4H), 7.71 (s, 2H), 2.23 (s, 6H), 1.81 (s, 6H). ^{13}C NMR (DMSO-d_6, 101 MHz) δ: 150.39, 149.68, 147.24, 137.83, 130.87, 128.38, 126.07, 124.47, 123.73, 20.08, 16.90.





Synthesis of M-1. To a solution of **A-5** (0.50 g, 1.25 mmol) in anhydrous Et_3N (12.50 mL) was added $POCl_3$ (0.70 mL, 7.5 mmol, 6 equiv). The resulting mixture was stirred at r.t. for 6 h. After that, deionized water (10 mL) was added slowly. The mixture was heated to 90 °C and reacted for additional 5 h. The mixture was then neutralized with Et_3N and filtered. The filter cake was washed with water for three times and dried under reduced pressure at 65 °C. After that, the white product (*R*)-5,5',6,6'-tetramethyl-3,3'-di(pyridin-4-yl)-1,1'-biphenyl-2,2'-hydrogen phosphate (**M-1**, 0.42 g, 73%) was obtained. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.65 (d, J = 4 Hz, 4H), 8.20 (d, J = 4 Hz, 4H), 7.45 (s, 2H), 2.37 (s, 6H), 2.04 (s, 6H). ^{13}C NMR (DMSO-d_6, 126 MHz) δ: 146.90, 145.58, 139.39, 133.40, 131.09, 129.89, 126.24, 107.65, 20.13, 17.85. ^{31}P NMR (DMSO-d_6, 202 MHz) δ: 0.86. ESI-MS calcd. For : 459.1474, found 459.1467. Elemental analysis: Calcd for $C_{26}H_{23}N_2O_4P$: C, 67.97%; H, 5.27%; N, 6.10%. Found: C, 68.02%; H, 5.20%; N, 6.12%. $[\alpha]_D^{20}$ = -29 (c = 1.0 MeCN).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8.20
8.19
7.45
2.36
2.04
4.00
3.94
2.01
6.03
6.00
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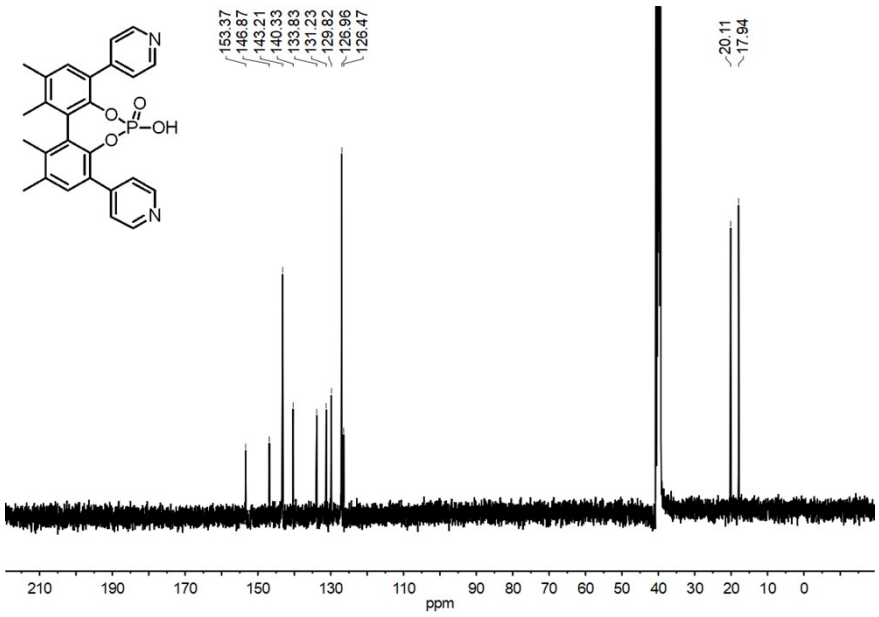
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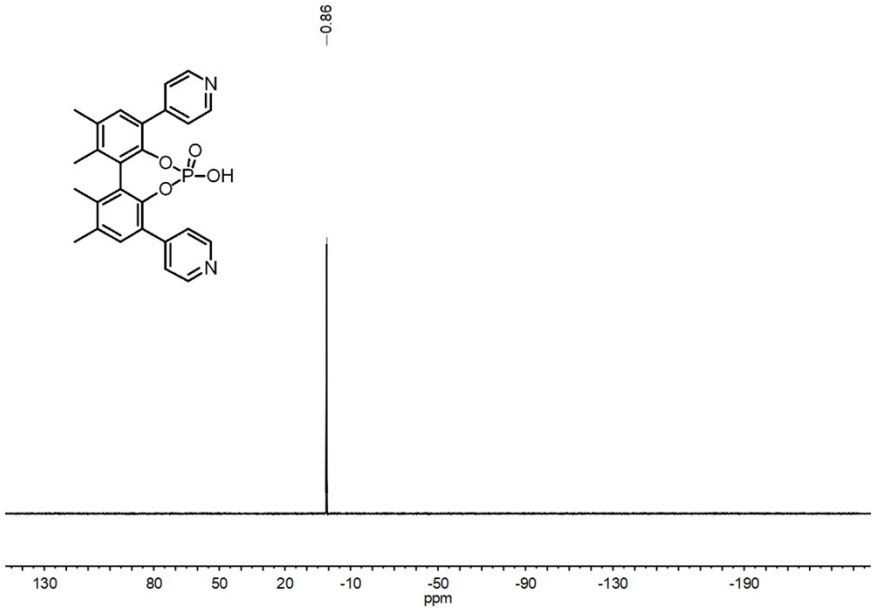
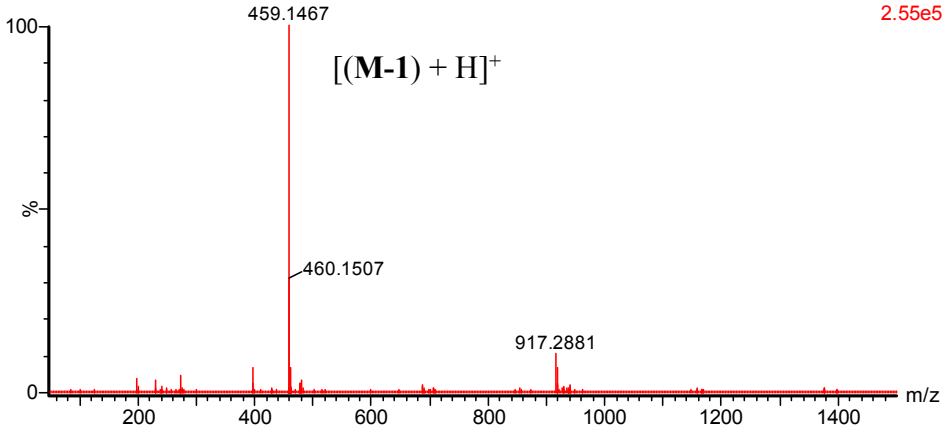
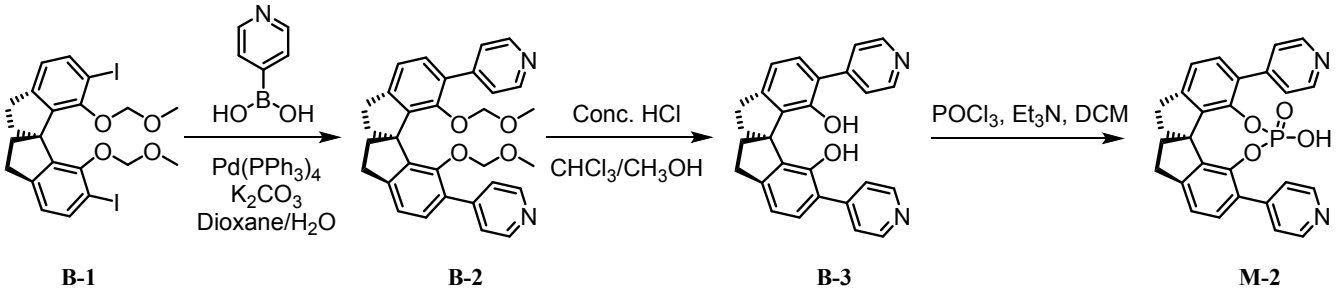
17.94
ppm



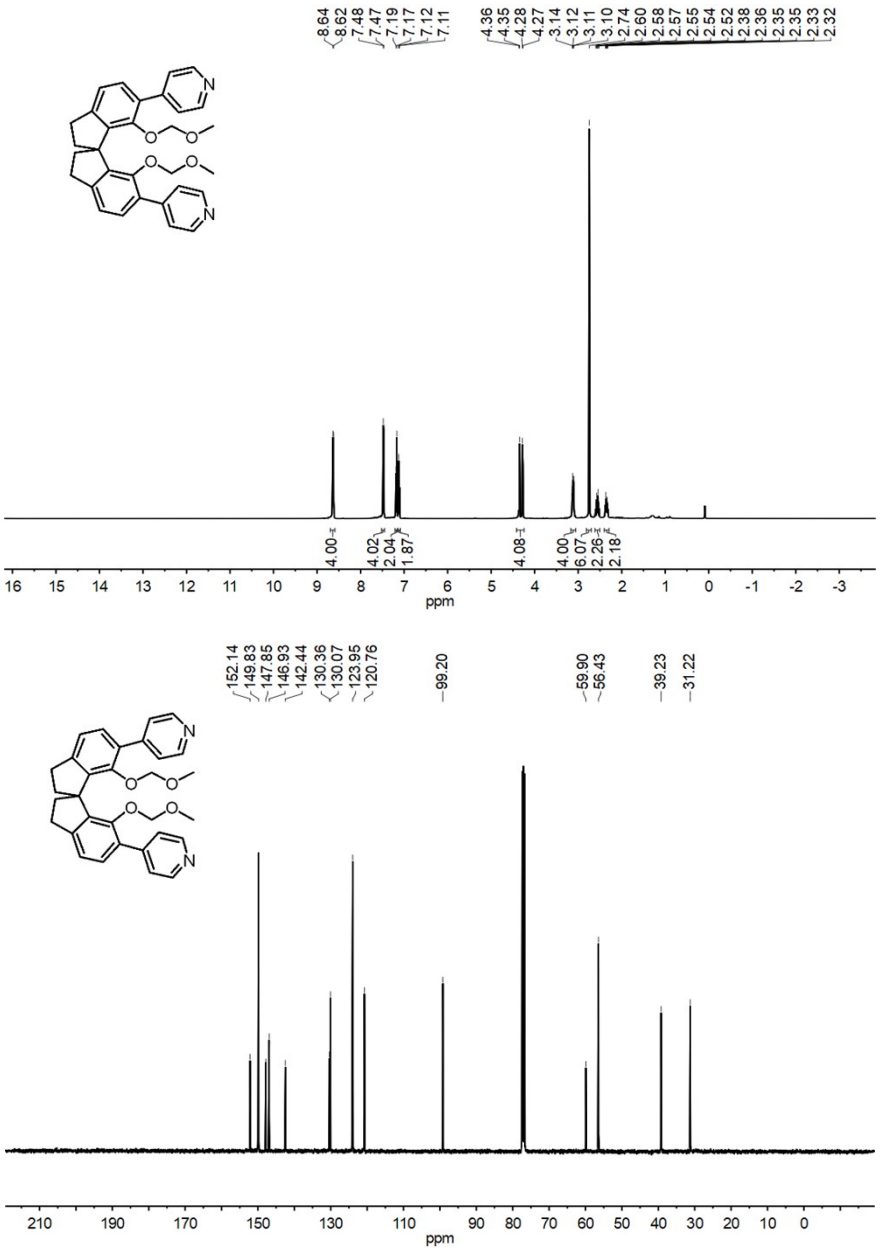




(*R*)-6,6′-diiodo-7,7′-bis(1-methoxymethoxy)-1,1′-spirobiindane (**B-1**) was synthesized according to the published procedure.[5]

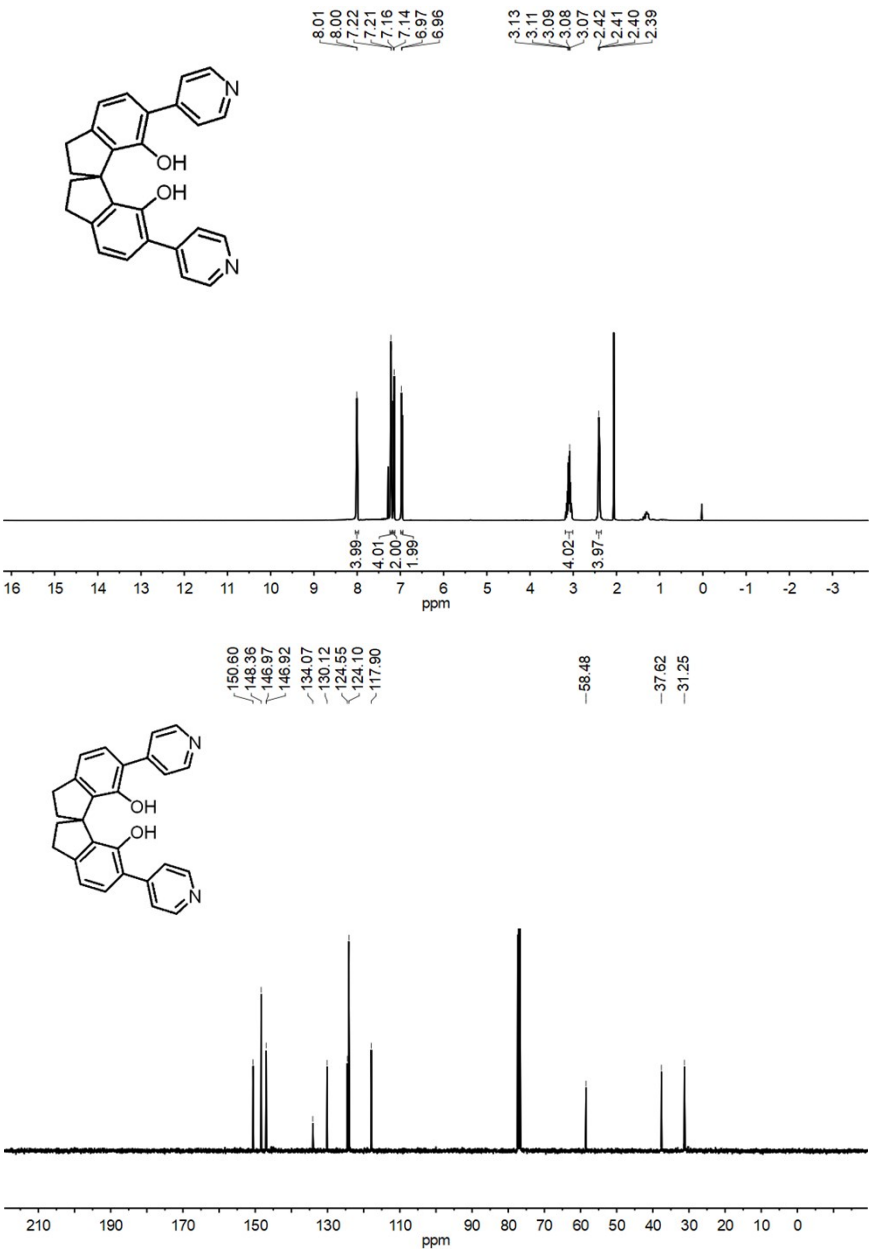
Synthesis of B-2. **B-1** (2.40 g, 4 mmol), 4-pyridylboronic acid (1.50 g, 12 mmol), K_2CO_3 (2.80 g, 20 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) were weighted into a two-neck 250 mL flask and the mixture was degassed for three times. 1,4-dioxane (100 mL) and H_2O (50 mL) were added under a N_2 atmosphere. The mixture was heated at 100 °C for 12 h with stirring. After cooling to room temperature, the resulting mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine,

dried over Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:1, v/v) to afford **B-2** as white solid (1.80 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.63 (d, *J* = 8 Hz, 4H), 7.47 (d, *J* = 4 Hz, 4H), 7.18 (d, *J* = 8 Hz, 2H), 7.11 (d, *J* = 4 Hz, 2H), 4.32 (dd, *J* = 32 Hz, 4 Hz, 4H), 3.12 (dd, *J* = 12 Hz, 8 Hz, 4H), 2.74 (s, 6H), 2.56 (m, 2H), 2.40-2.29 (m, 2H), ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 152.22, 149.83, 147.85, 147.00, 142.44, 130.36, 130.15, 120.76, 99.20, 76.97, 59.87, 56.43, 39.23, 31.22.



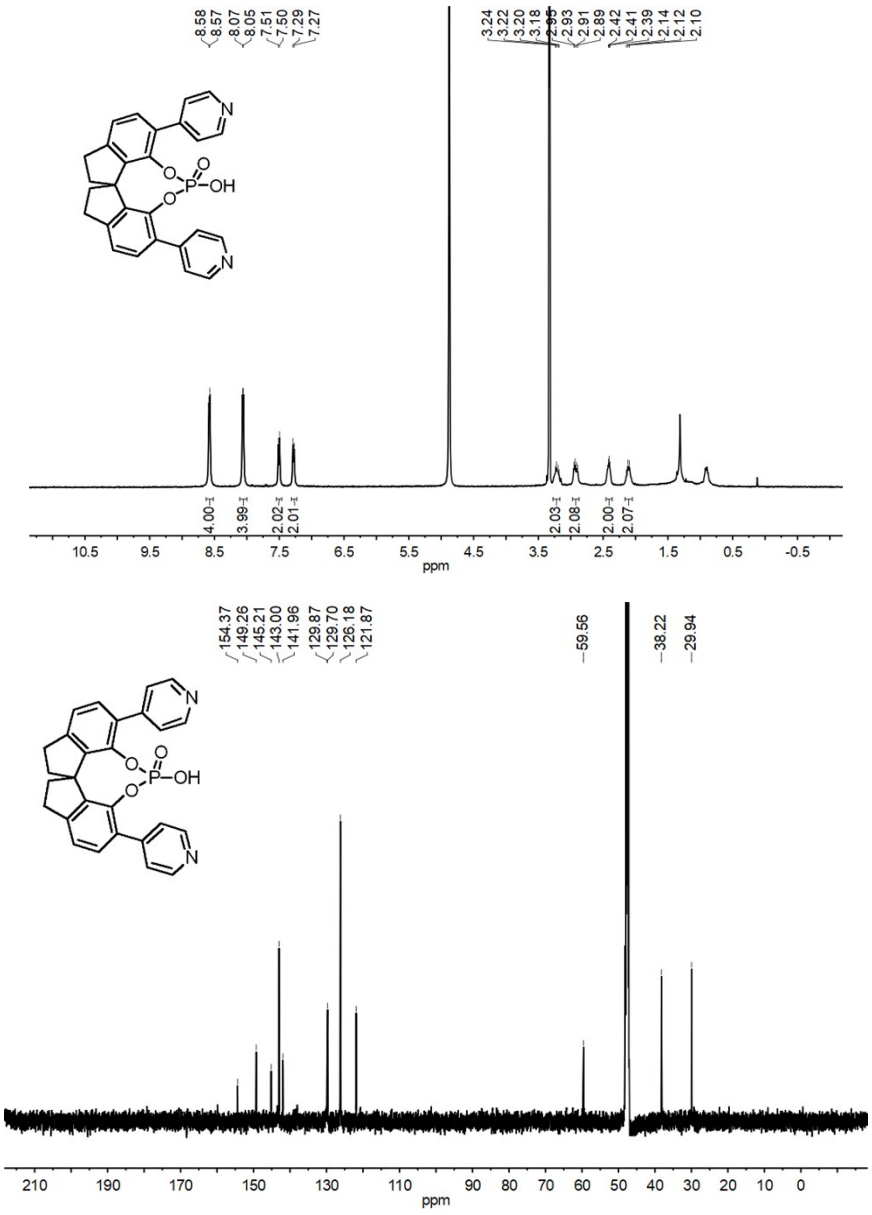
Synthesis of B-3. Concentrated HCl (6.5 mL, 6 M) was slowly added into a solution of **B-2** (1.40 g, 2.83 mmol) in 20 mL $CHCl_3$/MeOH (2:3, v/v), and the mixture was then stirred at room temperature for 10 h. The mixture was condensed under reduced pressure and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by preparative column (EtOAc/petroleum ether = 1/1) to give the compound **B-3** as white solid (1.13 g,

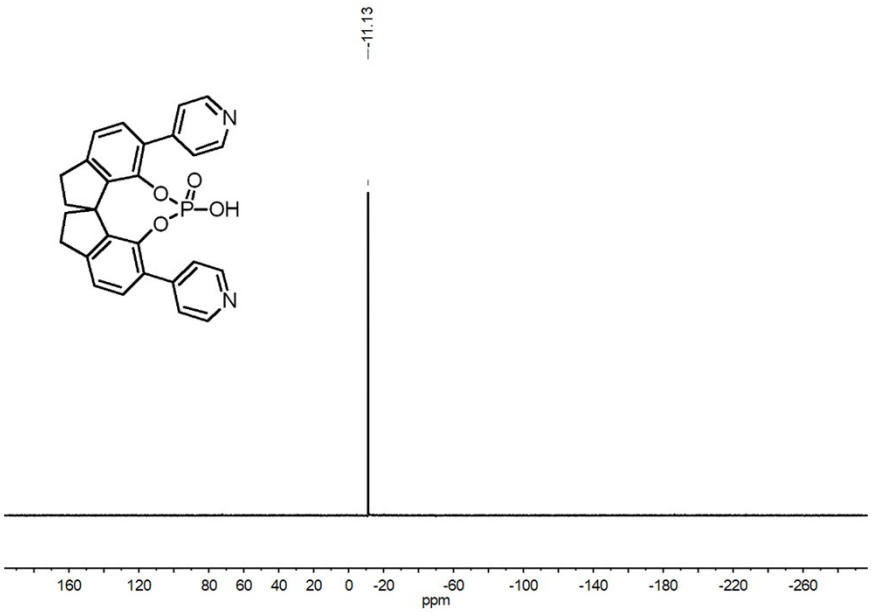
98%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, *J* = 4 Hz, 4H), 7.21 (d, *J* = 4 Hz, 4H), 7.15 (d, *J* = 8 Hz, 2H), 6.96 (d, *J* = 4 Hz, 2H), 3.18-3.01 (m, 4H), 2.42-2.39 (q, *J* = 4 Hz, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz,) δ 150.60, 148.36, 146.97, 146.92, 134.07, 130.12, 124.55, 124.10, 117.90, 58.48, 37.62, 31.25.

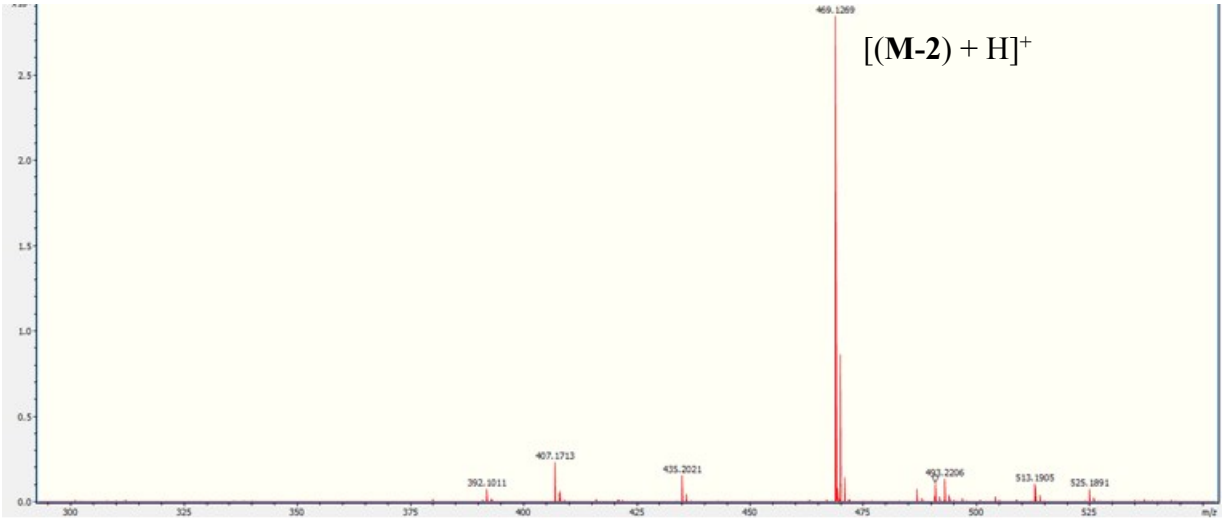


Synthesis of M-2. To a solution of **B-3** (0.48 g, 1.2 mmol) in anhydrous DCM, Et_3N (10 mL) and $POCl_3$ (0.67 mL, 7.54 mmol, 6 equiv) was added. The resulting mixture was stirred at r.t. for 6 h. After that, deionized water (10 mL) was added slowly. The mixture was heated to 90 °C and reacted for additional 5 h. The mixture was then neutralized with Et_3N and filtered. The filter cake was washed by water for three times and dried under reduced pressure at 65 °C. After that, The white product (**M-2**, 0.37 g, 66%) was obtained. ^{1}H NMR (CD_3OD_SPE, 400 MHz) δ 8.58 (d, *J* = 4 Hz, 4H), 8.06 (d, *J* = 8 Hz, 4H), 7.50 (d, *J* = 4 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 3.21 (q, *J* = 8 Hz, 2H), 2.92 (q, *J* = 8 Hz, 2H), 2.46-2.36 (m, 2H), 2.16-2.05 (m, 2H); ^{13}C NMR (CD_3OD_SPE, 126 MHz) δ 154.37, 149.26, 145.21,

143.00, 141.96, 129.87, 129.70, 126.18, 121.87, 59.56, 38.22, 29.94; ^{31}P NMR (CD_3OD_SPE, 202 MHz) δ: -11.13. ESI-MS calcd. For $C_{26}H_{23}N_2O_4P$ $[M+H]^+$: 469.4568, found 469.1269. Elemental analysis: Calcd for $C_{27}H_{21}N_2O_4P$: C, 69.08%; H, 4.72%; N, 5.97%. Found: C, 68.86%; H, 4.90%; N, 6.12%. $[\alpha]_D^{20}$ = 45 (*c* = 1.0 MeCN).







Synthesis of 1. A mixture of **M-1** (9.16 mg, 0.02 mmol), $Ca(OTf)_2$ (6.76 mg, 0.02 mmol), $Ca(BF_4)_2$ (3.11 mg, 0.02 mmol) in 1.5 mL acetonitrile was stirred at 70 ºC for 12 h. Colorless hexagonal prism-shaped crystals of **1** could be obtained in 80% yield (10.46 mg) by slow diffusion of CH_2Cl_2 into the solution at r.t for 2 days. FT-IR (KBr, cm^{-1}): 3421(m), 3246 (w), 2921(w), 1637(s), 1603(s), 1508(m), 1431(s), 1386(m), 1349(w), 1261(w), 1202(w), 1160(m), 1095(s), 1033(s), 873(s), 829(s), 789(w), 758(m), 735(m), 637(s), 577(w). Elemental analysis: Calcd for $C_{236}H_{285}O_{81}N_{18}P_9S_2F_6Ca$. C, 48.15%, H, 4.85%, N, 4.28%; Found: C, 46.32%, H, 4.92%, N, 3.38%.

Synthesis of 2. A mixture of **M-2** (9.36 mg, 0.02 mmol), $Pd(BF_4)_2(MeCN)_4$ (4.44 mg, 0.01 mmol) in 5.0 mL acetonitrile was stirred at 70 ºC for 1 day. Colorless block crystals of **2** was obtained in 87% yield by slow diffusion of 1, 2-dichlorobenzene into the solution at r.t. for 2 days. FT-IR (KBr, cm^{-1}): 3412(s), 3258 (w), 3108(w), 1634(s), 1607(s), 1543(w), 1509(s), 1453(s), 1385(w), 1268(s), 1218(s),

1093(s), 1026(s), 1000(s), 932(w), 861(s), 806(s), 765(s), 705(s), 646(m), 602(m), 552(m), 533(m). Elemental analysis: Calcd for $C_{81}H_{73}O_{17}N_6P_3$. C, 65.06%, H, 4.89%, N, 5.62%; Found: C, 62.74%, H, 4.92%, N, 4.32%.

3. Table S1. Crystal Data and Structure Refinement for 1 and **2**

Identification code	**1**	**2**
Empirical formula	$C_{236}H_{198}CaF_6N_{18}O_{81}P_9S_2$	$C_{81}H_{60}N_6O_{17}P_3$
Formula weight	5078.94	1482.26
Temperature (K)	173 K	173 K
Wavelength (Å)	0.71073	0.71073
Crystal system	Hexagonal	Tetragonal
Space group	$P6_322$	$I422$

Unit cell dimensions	a = 25.860(4) Å;
	b = 25.860(4) Å;
	c = 26.712(5) Å;
	α=90°; β=90°; γ=120°
		a = 26.422(4) Å;
		b = 26.422(4) Å;
		c = 30.839(6) Å;
		α=90°; β=90°; γ=90°

Volume (Å^3)	15470(5)	21269(20)
Z	2	8
Density (calculated) (mg/m^3)	1.090	0.915
Absorption coefficient (mm^{-1})	0.157	0.107
F(000)	5258	16251
Crystal color & shape	Colorless hexagonal prism	Colorless block
θ range for data collection (º)	1.186 to 25.560 deg.	2.626 to 25.986
Limiting indices	$0\leq h\leq 31$, $-26\leq k\leq 0$, $-32\leq l\leq 32$	$0\leq h\leq 32$, $-22\leq k\leq 23$, $0\leq l\leq 38$
Reflections collected	19265	10375
Independent reflections	9671 [R(int) = 0.0522]	10203 [R(int) = 0.0114]
Completeness	99.7%	95.8%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9671 / 2 / 538	10203 / 0 / 485
Goodness-of-fit on F^2	1.356	1.053
Final R indices [I>2sigma(I)]	R_1 = 0.1288, wR_2 = 0.3461	R_1 = 0.0750, wR_2 = 0.2202

R indices (all data)	R_1 = 0.1515, wR_2 = 0.3691	R_1 = 0.0754, wR_2 = 0.2209
Absolute structure parameter	0.40(6)	0.467(12)
Largest diff. peak and hole	0.755 and - 0.844 e.A^{-3}	1.162 and -0.402 e.A^{-3}

4. Bond lengths [Å] and angles [º]

Table S2. Bond lengths [Å] and angles [º] for 1

P(2)-O(5)	1.606(6)	C(19)-C(20)	1.506(15)
P(2)-O(5)#1	1.606(6)	C(19)-C(17)	1.351(16)
P(2)-O(6)#1	1.483(6)	C(20)-C(21)	1.337(14)
P(2)-O(6)	1.483(6)	C(33)-C(34)	1.332(14)
P(1)-O(1)	1.608(7)	C(30)-C(31)	1.346(15)
P(1)-O(3)	1.505(7)	C(17)-C(18)	1.576(17)
P(1)-O(2)	1.591(7)	C(17)-C(15)	1.325(16)
P(1)-O(4)	1.514(7)	C(34)-C(36)	1.444(16)
O(1)-C(13)	1.428(12)	C(34)-C(35)	1.536(15)
O(5)-C(39)	1.428(10)	C(5)-C(4)	1.331(13)
O(2)-C(21)	1.430(12)	C(37)-C(36)	1.555(15)
N(2)-C(26)	1.339(15)	C(24)-C(23)	1.297(19)
N(2)-C(24)	1.286(18)	C(21)-C(14)	1.369(14)
N(1)-C(1)	1.351(14)	C(13)-C(12)	1.335(14)
N(1)-C(5)	1.335(13)	C(13)-C(6)	1.377(14)
C(3)-C(2)	1.362(14)	C(15)-C(14)	1.436(16)
C(3)-C(4)	1.405(15)	C(15)-C(16)	1.549(16)
C(3)-C(6)	1.481(14)	C(8)-C(10)	1.343(15)
C(32)-C(39)	1.367(14)	C(8)-C(9)	1.490(17)
C(32)-C(29)	1.416(15)	C(12)-C(10)	1.429(14)
C(32)-C(33)	1.447(14)	C(12)-C(14)	1.531(15)
N(3)-C(31)	1.325(14)	C(10)-C(11)	1.519(15)
N(3)-C(27)	1.332(16)	Ca(1)-O(7)#2	2.275(18)
C(39)-C(38)	1.397(13)	Ca(1)-O(7)#3	2.275(18)
C(29)-C(28)	1.407(15)	Ca(1)-O(7)#4	2.275(18)
C(29)-C(30)	1.478(14)	Ca(1)-O(7)	2.275(18)
C(38)-C(38)#1	1.495(19)	Ca(1)-O(7)#5	2.275(18)
C(38)-C(36)	1.331(15)	Ca(1)-O(7)#6	2.275(18)

C(1)-C(2)	1.357(15)	S(1)-O(14)#6	1.427(8)
C(26)-C(25)	1.307(15)	S(1)-O(14)	1.427(7)
C(7)-C(8)	1.458(16)	S(1)-O(14)#4	1.428(7)
C(7)-C(6)	1.405(15)	S(1)-C(40)	1.83(3)
C(22)-C(25)	1.385(15)	C(40)-F(1)#4	1.374(17)
C(22)-C(20)	1.459(15)	C(40)-F(1)	1.374(17)
C(22)-C(23)	1.383(15)	C(40)-F(1)#6	1.374(17)

O(5)-P(2)-O(5)#1	101.9(5)	C(34)-C(36)-C(37)	112.5(9)
O(6)-P(2)-O(5)#1	111.0(3)	N(2)-C(24)-C(23)	126.5(12)
O(6)#1-P(2)-O(5)	111.0(3)	C(20)-C(21)-O(2)	117.2(9)
O(6)#1-P(2)-O(5)#1	104.7(3)	C(20)-C(21)-C(14)	127.7(10)
O(6)-P(2)-O(5)	104.7(3)	C(14)-C(21)-O(2)	114.7(8)
O(6)#1-P(2)-O(6)	121.8(5)	C(12)-C(13)-O(1)	117.0(8)
O(3)-P(1)-O(1)	103.5(4)	C(12)-C(13)-C(6)	123.8(9)
O(3)-P(1)-O(2)	113.0(4)	C(6)-C(13)-O(1)	119.2(9)
O(3)-P(1)-O(4)	120.0(4)	C(17)-C(15)-C(14)	121.1(11)
O(2)-P(1)-O(1)	101.3(3)	C(17)-C(15)-C(16)	119.3(11)
O(4)-P(1)-O(1)	112.6(4)	C(14)-C(15)-C(16)	119.6(11)
O(4)-P(1)-O(2)	105.1(4)	N(3)-C(31)-C(30)	125.8(11)
C(13)-O(1)-P(1)	115.5(6)	C(7)-C(8)-C(9)	110.3(11)
C(39)-O(5)-P(2)	116.9(6)	C(10)-C(8)-C(7)	122.1(10)
C(21)-O(2)-P(1)	118.8(6)	C(10)-C(8)-C(9)	127.6(11)
C(24)-N(2)-C(26)	114.3(11)	C(5)-C(4)-C(3)	119.5(10)
C(5)-N(1)-C(1)	119.4(9)	C(13)-C(12)-C(10)	119.6(9)
C(2)-C(3)-C(4)	116.5(9)	C(13)-C(12)-C(14)	118.4(9)
C(2)-C(3)-C(6)	122.6(10)	C(10)-C(12)-C(14)	121.9(9)
C(4)-C(3)-C(6)	120.8(9)	C(7)-C(6)-C(3)	118.0(10)
C(39)-C(32)-C(29)	126.5(9)	C(13)-C(6)-C(3)	123.3(9)
C(39)-C(32)-C(33)	112.2(10)	C(13)-C(6)-C(7)	118.7(9)
C(29)-C(32)-C(33)	121.2(10)	C(8)-C(10)-C(12)	118.5(9)
C(31)-N(3)-C(27)	116.4(10)	C(8)-C(10)-C(11)	118.9(10)
C(32)-C(39)-O(5)	117.1(8)	C(12)-C(10)-C(11)	122.6(10)
C(32)-C(39)-C(38)	126.6(9)	C(21)-C(14)-C(15)	115.8(10)

C(38)-C(39)-O(5)	116.2(8)	C(21)-C(14)-C(12)	120.0(9)
C(32)-C(29)-C(30)	122.2(9)	C(15)-C(14)-C(12)	124.1(10)
C(28)-C(29)-C(32)	123.8(10)	C(28)-C(27)-N(3)	124.5(12)
C(28)-C(29)-C(30)	113.9(9)	C(24)-C(23)-C(22)	119.6(12)
C(39)-C(38)-C(38)#1	118.4(7)	O(7)#5-Ca(1)-O(7)#4	94.9(7)
C(36)-C(38)-C(39)	117.6(9)	O(7)#5-Ca(1)-O(7)#3	89.3(4)
C(36)-C(38)-C(38)#1	123.9(8)	O(7)#2-Ca(1)-O(7)	94.9(7)
N(1)-C(1)-C(2)	119.3(10)	O(7)#2-Ca(1)-O(7)#3	89.3(4)
C(25)-C(26)-N(2)	125.0(12)	O(7)#2-Ca(1)-O(7)#5	89.3(4)
C(6)-C(7)-C(8)	116.9(10)	O(7)#4-Ca(1)-O(7)#3	86.8(6)
C(25)-C(22)-C(20)	122.3(10)	O(7)-Ca(1)-O(7)#5	86.8(6)
C(23)-C(22)-C(25)	115.3(10)	O(7)#6-Ca(1)-O(7)#4	89.3(4)
C(23)-C(22)-C(20)	122.2(10)	O(7)#2-Ca(1)-O(7)#6	86.8(6)
C(27)-C(28)-C(29)	122.3(11)	O(7)-Ca(1)-O(7)#3	174.2(8)
C(17)-C(19)-C(20)	120.8(10)	O(7)#5-Ca(1)-O(7)#6	174.2(8)
C(1)-C(2)-C(3)	122.4(10)	O(7)#6-Ca(1)-O(7)#3	94.9(7)
C(26)-C(25)-C(22)	119.1(12)	O(7)#2-Ca(1)-O(7)#4	174.2(8)
C(22)-C(20)-C(19)	119.7(9)	O(7)-Ca(1)-O(7)#4	89.3(4)
C(21)-C(20)-C(22)	127.0(10)	O(7)-Ca(1)-O(7)#6	89.3(4)
C(21)-C(20)-C(19)	112.9(10)	O(14)#4-S(1)-O(14)#6	117.3(3)
C(34)-C(33)-C(32)	124.5(10)	O(14)#4-S(1)-O(14)	117.3(3)
C(31)-C(30)-C(29)	116.8(10)	O(14)#6-S(1)-O(14)	117.3(3)
C(19)-C(17)-C(18)	115.9(10)	O(14)#4-S(1)-C(40)	99.5(5)
C(15)-C(17)-C(19)	121.7(11)	O(14)#6-S(1)-C(40)	99.5(5)
C(15)-C(17)-C(18)	122.4(11)	O(14)-S(1)-C(40)	99.5(5)
C(33)-C(34)-C(36)	117.9(9)	F(1)#4-C(40)-S(1)	112.2(13)
C(33)-C(34)-C(35)	119.6(10)	F(1)#6-C(40)-S(1)	112.2(13)
C(36)-C(34)-C(35)	122.5(10)	F(1)-C(40)-S(1)	112.2(13)
C(4)-C(5)-N(1)	122.7(10)	F(1)#6-C(40)-F(1)	106.6(14)
C(38)-C(36)-C(34)	121.1(10)	F(1)#6-C(40)-F(1)#4	106.6(14)
C(38)-C(36)-C(37)	126.0(11)	F(1)#4-C(40)-F(1)	106.6(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y,y,-z+3/2 #2 -y+1,-x+1,-z+1/2 #3 -x+y+1,y,-z+1/2 #4 -y+1,x-y,z #5 x,x-y,-z+1/2 #6 -x+y+1,-x+1,z

Table S3. Bond lengths [Å] and angles [º] for 2

P(1)-O(2)	1.619(3)	C(20)-C(21)	1.366(7)
P(1)-O(4)	1.474(3)	C(19)-C(7)	1.474(6)
P(1)-O(1)	1.616(3)	C(16)-C(15)	1.401(7)
P(1)-O(3)	1.477(3)	C(16)-C(24)	1.475(7)
P(2)-O(5)#1	1.628(3)	C(15)-C(14)	1.379(7)
P(2)-O(5)	1.628(3)	C(38)-C(37)	1.539(7)
P(2)-O(6)#1	1.485(3)	C(29)-C(30)	1.394(7)
P(2)-O(6)	1.485(3)	C(29)-C(2)	1.495(8)
O(2)-C(12)	1.398(5)	C(29)-C(33)	1.406(7)
O(5)-C(1)	1.380(6)	C(7)-C(8)	1.413(7)
O(1)-C(17)	1.406(5)	C(24)-C(28)	1.409(9)
N(1)-C(23)	1.337(6)	C(24)-C(25)	1.390(9)
N(1)-C(21)	1.340(6)	C(30)-C(31)	1.381(7)
C(18)-C(13)	1.389(6)	C(6)-C(34)	1.520(6)
C(18)-C(17)	1.396(6)	C(6)-C(5)	1.398(7)
C(18)-C(39)	1.515(6)	C(2)-C(3)	1.391(8)
C(13)-C(14)	1.373(6)	C(40)-C(41)	1.525(6)
C(13)-C(41)	1.507(6)	C(10)-C(9)	1.398(7)
N(3)-C(31)	1.346(7)	C(10)-C(37)	1.494(6)
N(3)-C(32)	1.343(8)	C(33)-C(32)	1.383(9)
C(17)-C(16)	1.384(6)	C(3)-C(4)	1.390(9)
C(1)-C(6)	1.393(7)	C(34)-C(6)#1	1.520(6)
C(1)-C(2)	1.420(7)	C(34)-C(35)	1.532(7)
C(23)-C(22)	1.371(6)	C(34)-C(35)#1	1.532(7)
C(39)-C(11)	1.535(6)	C(8)-C(9)	1.390(7)
C(39)-C(38)	1.550(5)	C(28)-C(27)	1.317(10)
C(39)-C(40)	1.544(6)	C(5)-C(4)	1.371(9)
C(11)-C(12)	1.358(6)	C(5)-C(36)	1.519(9)
C(11)-C(10)	1.402(6)	C(25)-C(26)	1.382(10)
C(12)-C(7)	1.412(6)	C(35)-C(36)	1.537(10)
C(22)-C(19)	1.415(6)	N(2)-C(26)	1.359(12)
C(20)-C(19)	1.395(6)	N(2)-C(27)	1.351(12)

O(4)-P(1)-O(2)	104.59(17)	C(15)-C(16)-C(24)	118.6(4)
O(4)-P(1)-O(1)	110.87(17)	C(14)-C(15)-C(16)	122.2(4)
O(4)-P(1)-O(3)	120.9(2)	C(37)-C(38)-C(39)	104.4(3)
O(1)-P(1)-O(2)	103.27(16)	C(30)-C(29)-C(2)	122.5(4)
O(3)-P(1)-O(2)	110.42(18)	C(30)-C(29)-C(33)	118.4(5)
O(3)-P(1)-O(1)	105.51(17)	C(33)-C(29)-C(2)	119.1(4)
O(5)-P(2)-O(5)#1	101.2(2)	C(12)-C(7)-C(19)	125.1(4)
O(6)#1-P(2)-O(5)#1	105.13(16)	C(12)-C(7)-C(8)	117.1(4)
O(6)#1-P(2)-O(5)	110.95(15)	C(8)-C(7)-C(19)	117.8(4)
O(6)-P(2)-O(5)#1	110.95(15)	C(28)-C(24)-C(16)	121.8(6)
O(6)-P(2)-O(5)	105.14(16)	C(25)-C(24)-C(16)	122.7(5)
O(6)#1-P(2)-O(6)	121.6(3)	C(25)-C(24)-C(28)	115.5(6)
C(12)-O(2)-P(1)	119.1(3)	C(31)-C(30)-C(29)	119.6(4)
C(1)-O(5)-P(2)	116.9(3)	C(1)-C(6)-C(34)	131.9(5)
C(17)-O(1)-P(1)	116.2(3)	C(1)-C(6)-C(5)	118.4(5)
C(23)-N(1)-C(21)	120.6(4)	C(5)-C(6)-C(34)	109.6(5)
C(13)-C(18)-C(17)	119.5(4)	C(1)-C(2)-C(29)	120.0(4)
C(13)-C(18)-C(39)	109.9(4)	C(3)-C(2)-C(1)	119.3(5)
C(17)-C(18)-C(39)	130.5(4)	C(3)-C(2)-C(29)	120.7(5)
C(18)-C(13)-C(41)	110.6(4)	C(41)-C(40)-C(39)	105.3(3)
C(14)-C(13)-C(18)	121.0(4)	C(13)-C(14)-C(15)	118.7(5)
C(14)-C(13)-C(41)	128.4(4)	N(3)-C(31)-C(30)	120.9(5)
C(32)-N(3)-C(31)	120.8(5)	C(13)-C(41)-C(40)	102.1(3)
C(18)-C(17)-O(1)	117.5(4)	C(11)-C(10)-C(37)	111.9(4)
C(16)-C(17)-O(1)	121.9(4)	C(9)-C(10)-C(11)	119.5(4)
C(16)-C(17)-C(18)	120.5(4)	C(9)-C(10)-C(37)	128.6(4)
O(5)-C(1)-C(6)	117.8(4)	C(32)-C(33)-C(29)	119.1(5)
O(5)-C(1)-C(2)	121.4(4)	C(4)-C(3)-C(2)	119.7(5)
C(6)-C(1)-C(2)	120.5(5)	C(6)#1-C(34)-C(6)	120.2(6)
N(1)-C(23)-C(22)	121.0(4)	C(6)#1-C(34)-C(35)#1	100.5(3)
C(18)-C(39)-C(11)	123.3(4)	C(6)-C(34)-C(35)#1	112.6(3)
C(18)-C(39)-C(38)	112.3(3)	C(6)#1-C(34)-C(35)	112.6(3)
C(18)-C(39)-C(40)	100.5(3)	C(6)-C(34)-C(35)	100.5(3)

C(11)-C(39)-C(38)	100.5(3)	C(35)-C(34)-C(35)#1	110.7(6)
C(11)-C(39)-C(40)	110.7(3)	N(3)-C(32)-C(33)	121.1(5)
C(40)-C(39)-C(38)	109.4(3)	C(9)-C(8)-C(7)	121.7(4)
C(12)-C(11)-C(39)	131.2(4)	C(8)-C(9)-C(10)	119.2(5)
C(12)-C(11)-C(10)	120.9(4)	C(10)-C(37)-C(38)	102.2(4)
C(10)-C(11)-C(39)	107.7(4)	C(27)-C(28)-C(24)	122.8(8)
O(2)-C(12)-C(7)	119.7(4)	C(6)-C(5)-C(36)	109.8(5)
C(11)-C(12)-O(2)	118.9(4)	C(4)-C(5)-C(6)	121.3(5)
C(11)-C(12)-C(7)	121.4(4)	C(4)-C(5)-C(36)	128.7(6)
C(23)-C(22)-C(19)	119.7(4)	C(26)-C(25)-C(24)	119.0(7)
C(21)-C(20)-C(19)	120.0(4)	C(34)-C(35)-C(36)	104.8(4)
C(22)-C(19)-C(7)	121.2(4)	C(5)-C(4)-C(3)	120.7(5)
C(20)-C(19)-C(22)	117.2(4)	C(27)-N(2)-C(26)	116.3(7)
C(20)-C(19)-C(7)	121.4(4)	C(5)-C(36)-C(35)	101.8(5)
N(1)-C(21)-C(20)	121.4(4)	N(2)-C(26)-C(25)	123.7(8)
C(17)-C(16)-C(15)	117.9(4)	C(28)-C(27)-N(2)	122.7(8)
C(17)-C(16)-C(24)	123.5(4)		

#1 -y+1,-x+1,-z+1

5. Additional X-ray Crystallographic Structures

Figure S1. The asymmetric unit: a) 1, b) 2. (violet, Ca; sky-blue, N; green, P; yellow, S; bright-green, F; gray, C; red, O)

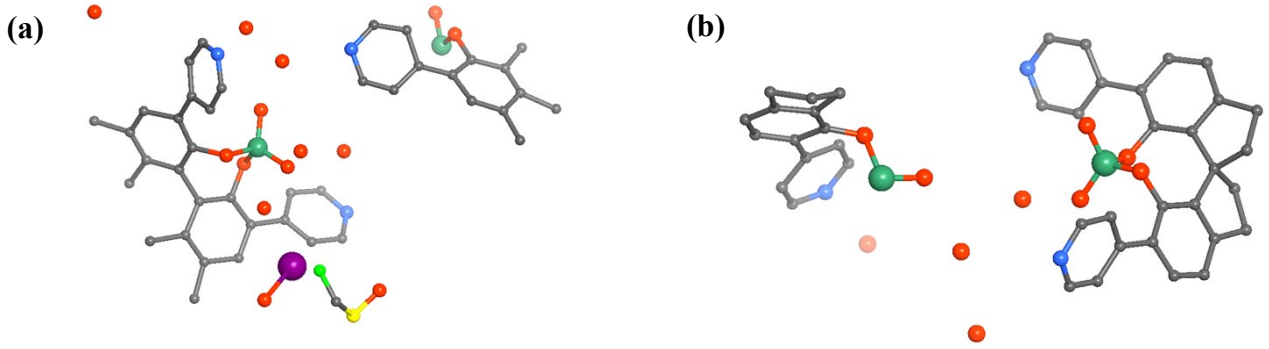


Figure S2. C_3 symmetric chiral cages in 1 viewed along the a-axis (a) and c-axis (b). (violet, Ca; sky-blue, N; green, P; yellow, S; bright-green, F; gray, C; red, O)

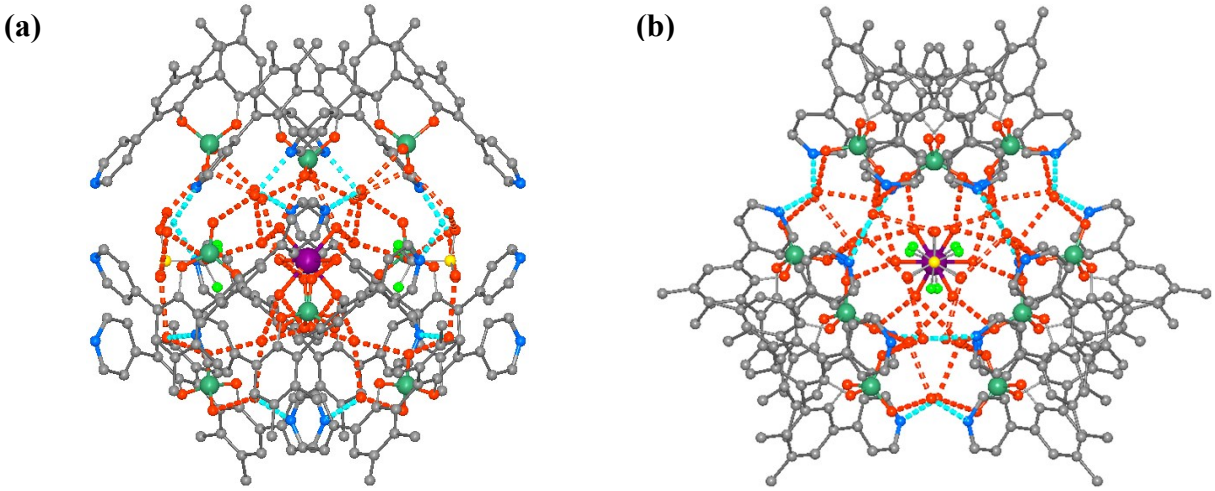


Figure S3. C_4 symmetric chiral cages in 2 viewed along the a-axis (a) and c-axis (b). (sky-blue, N; green, P; gray, C; red, O)

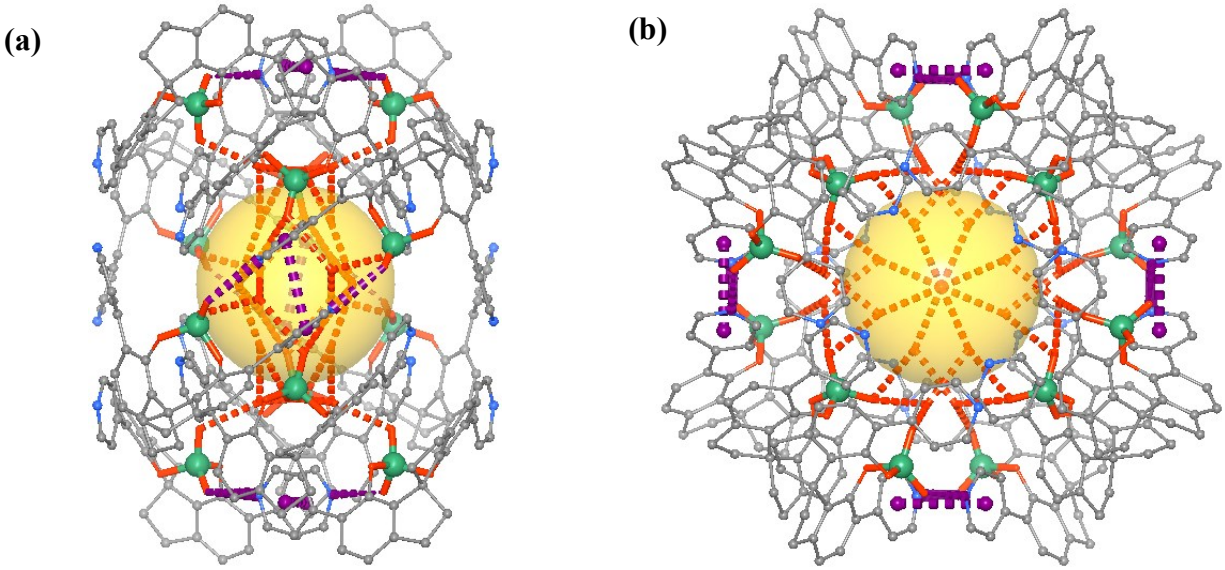
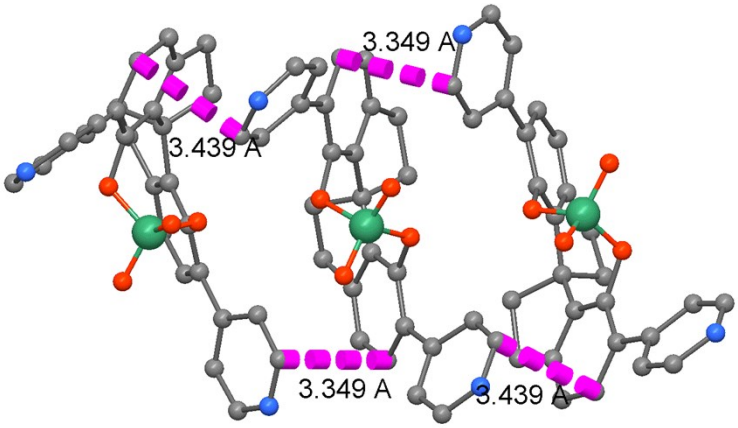
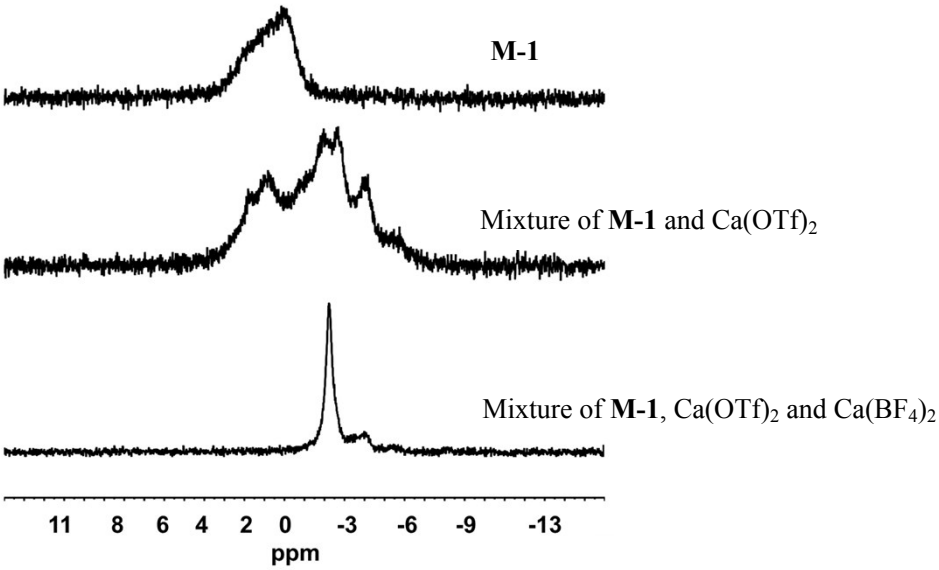


Figure S4. π-π interaction in 3D structure of 2. (sky-blue, N; green, P; gray, C; red, O)

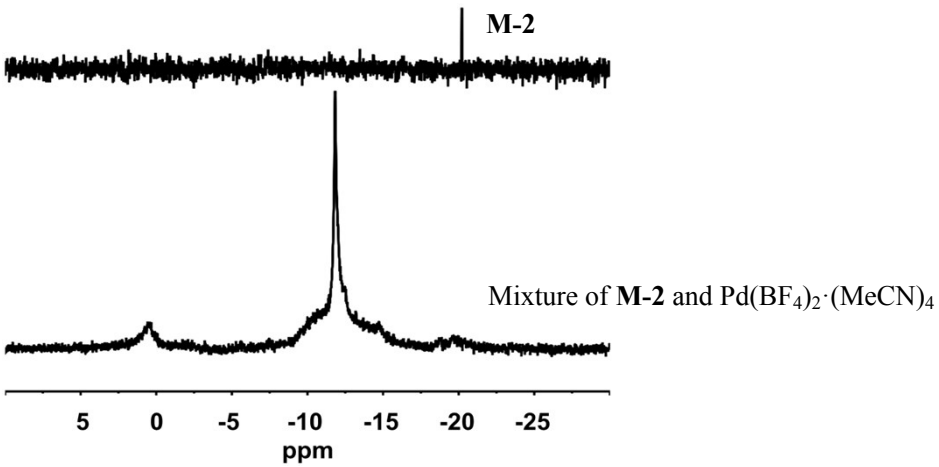


6. Figure S5. ^{31}P NMR spectra

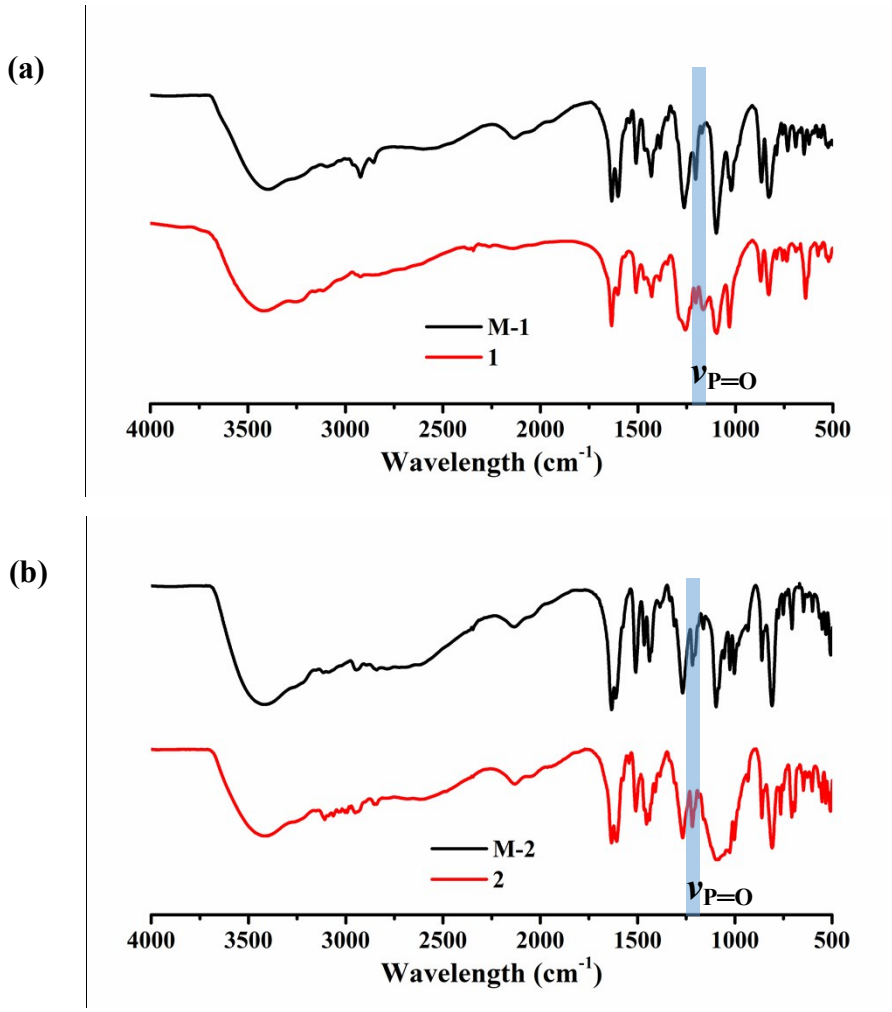
(a)



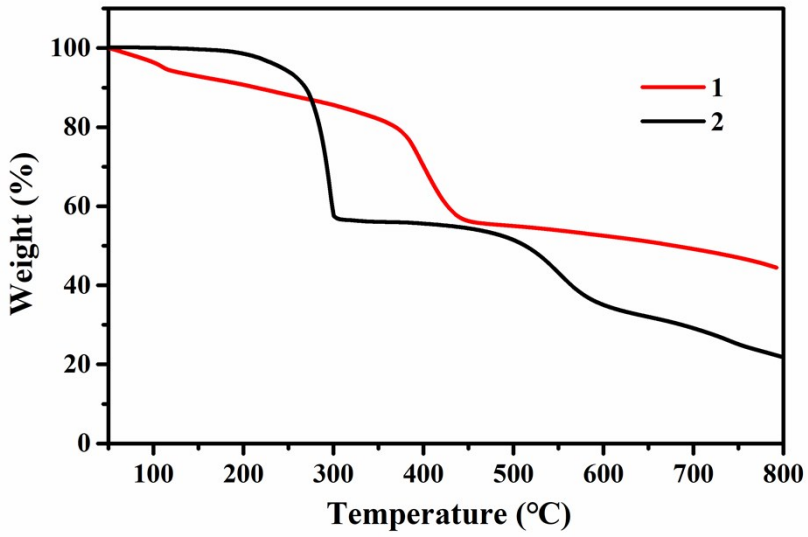
(b)



7. Figure S6. FT-IR Spectra (a) M-1 and 1, (b) M-2 and 2.

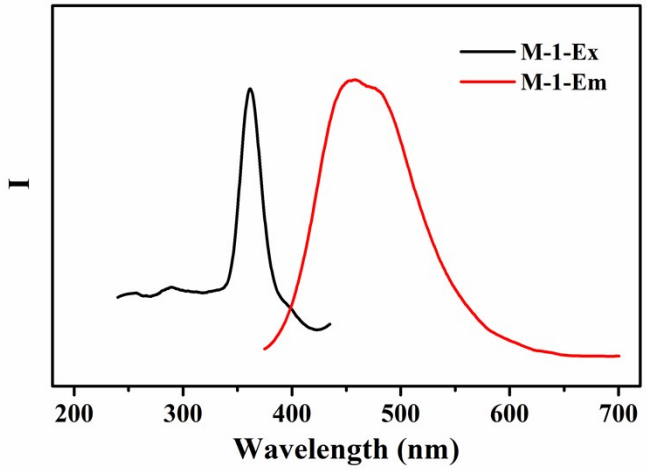


8. Figure S7. TGA curves.

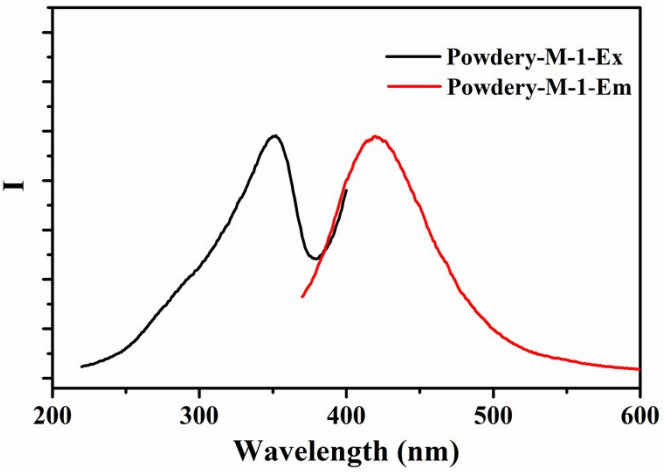


9. Figure S8. Fluorescence Spectra of (a) M-1 in CH_3CN (c = 5 mM); (b) Powdery M-1; (c) 1 in CH_3CN (c = 5 mM); (d) Crystalline 1; (e) M-2 in CH_3CN (c = 5 mM); (f) Powdery M-2; (g) 2 in CH_3CN (c = 5 mM); (h) Crystalline 2.

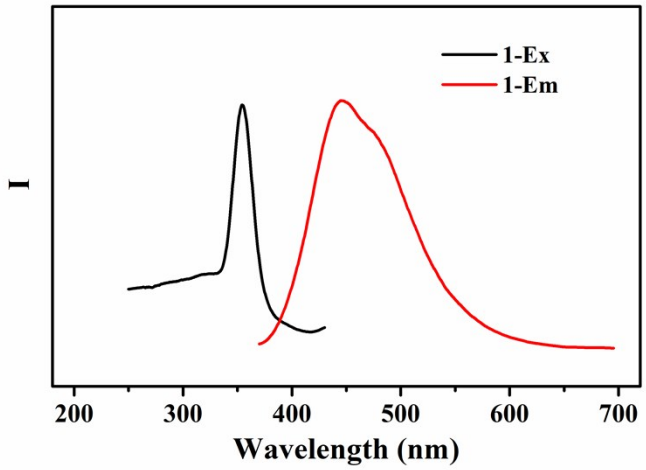
(a)



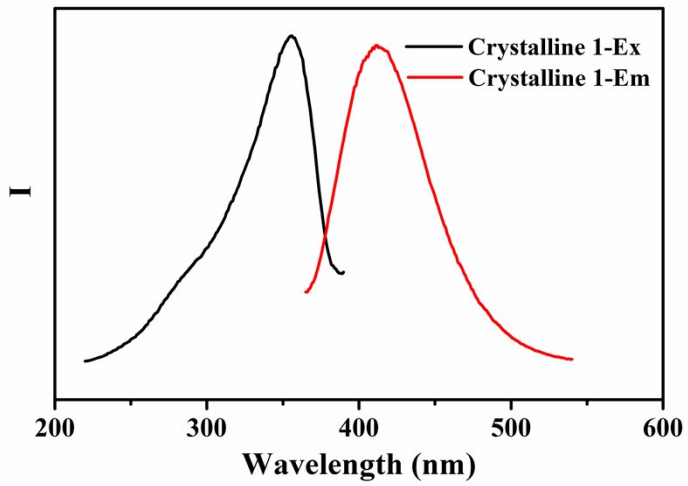
(b)



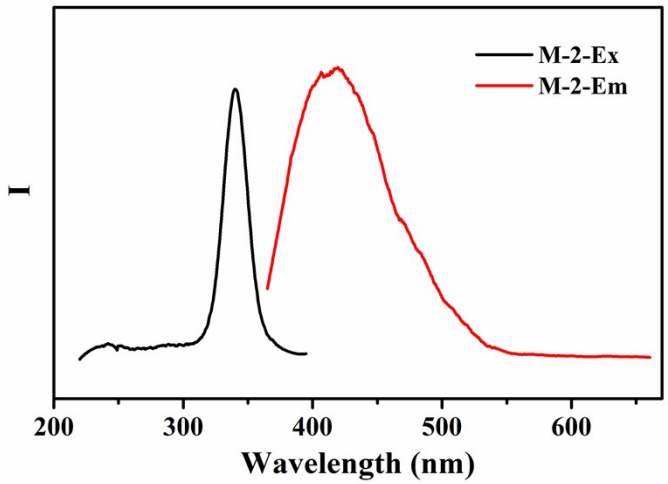
(c)



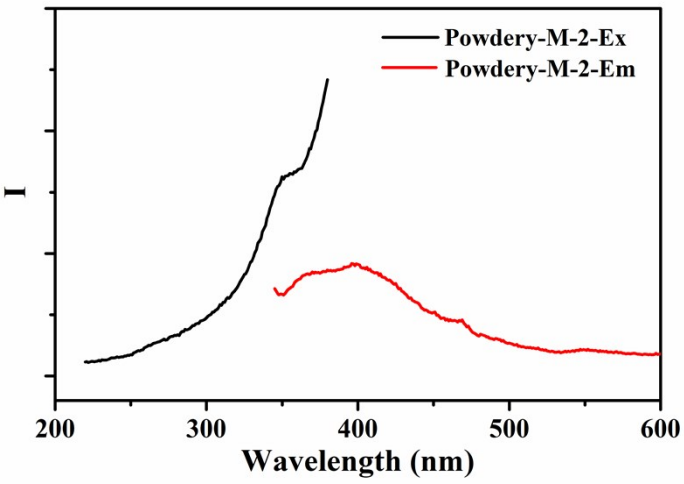
(d)

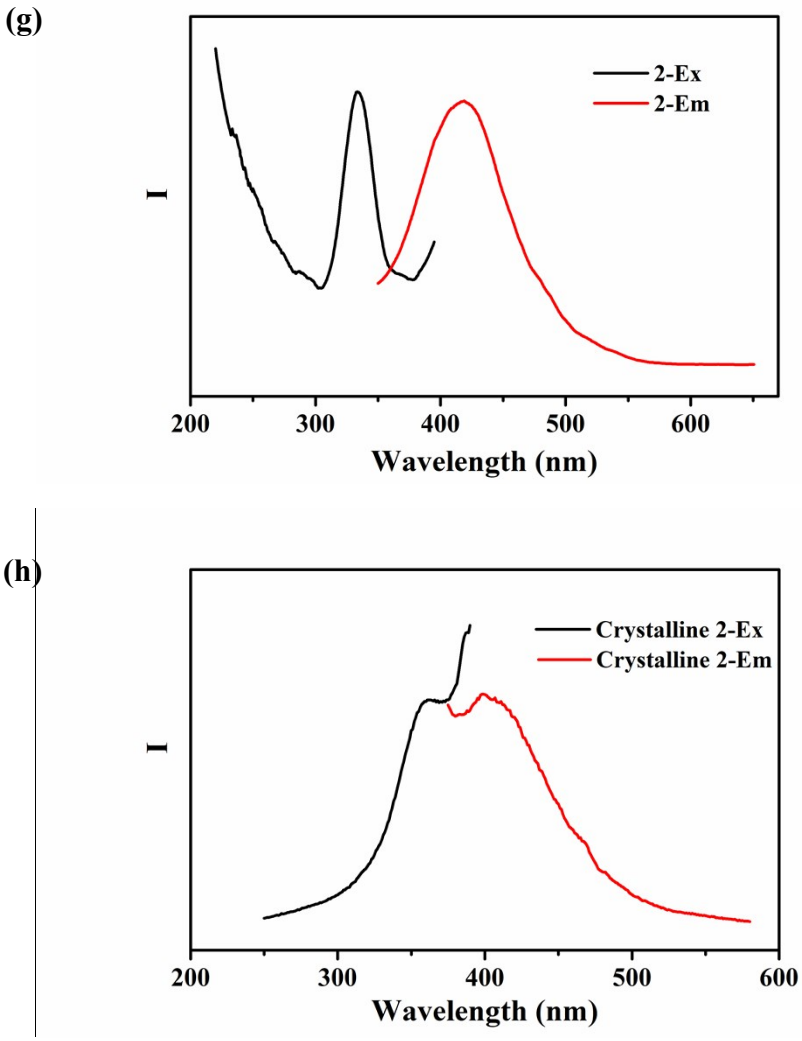

Crystalline 1-Ex
Crystalline 1-Em
I
200
300
400
500
600
Wavelength (nm)

(e)


M-2-Ex
M-2-Em
I
200
300
400
500
600
Wavelength (nm)

(f)


Powdery-M-2-Ex
Powdery-M-2-Em
I
200
300
400
500
600
Wavelength (nm)



10. Figure S9. Quantum yields[6].

QY is calculated by measuring the sample inside an integrating sphere. To calculate the QY a clean sample holder is measured as reference and afterwards the sample is measured. The scattered photons at the excitation wavelength range are used to calculate the number of photons absorbed by the sample, by comparing the number of photons scattered by the clean sample holder (Ex − Clean) and by the sample (Ex − Sample). The number of emitted photons is calculated by integrating the number of photons emitted by the sample (Em − Sample) subtracted by the noise level (Em − Clean). The QY is defined by the ratio of emitted photons and absorbed photons.

$$QY(\%) = \frac{\#\ of\ emittied\ photons}{\#\ of\ absorbed\ photons} \cdot 100 = \frac{sum(Em - Sample) - sum(Em - Clean)}{sum(Ex - Clean) - sum(Ex - Sample)} \cdot 100$$

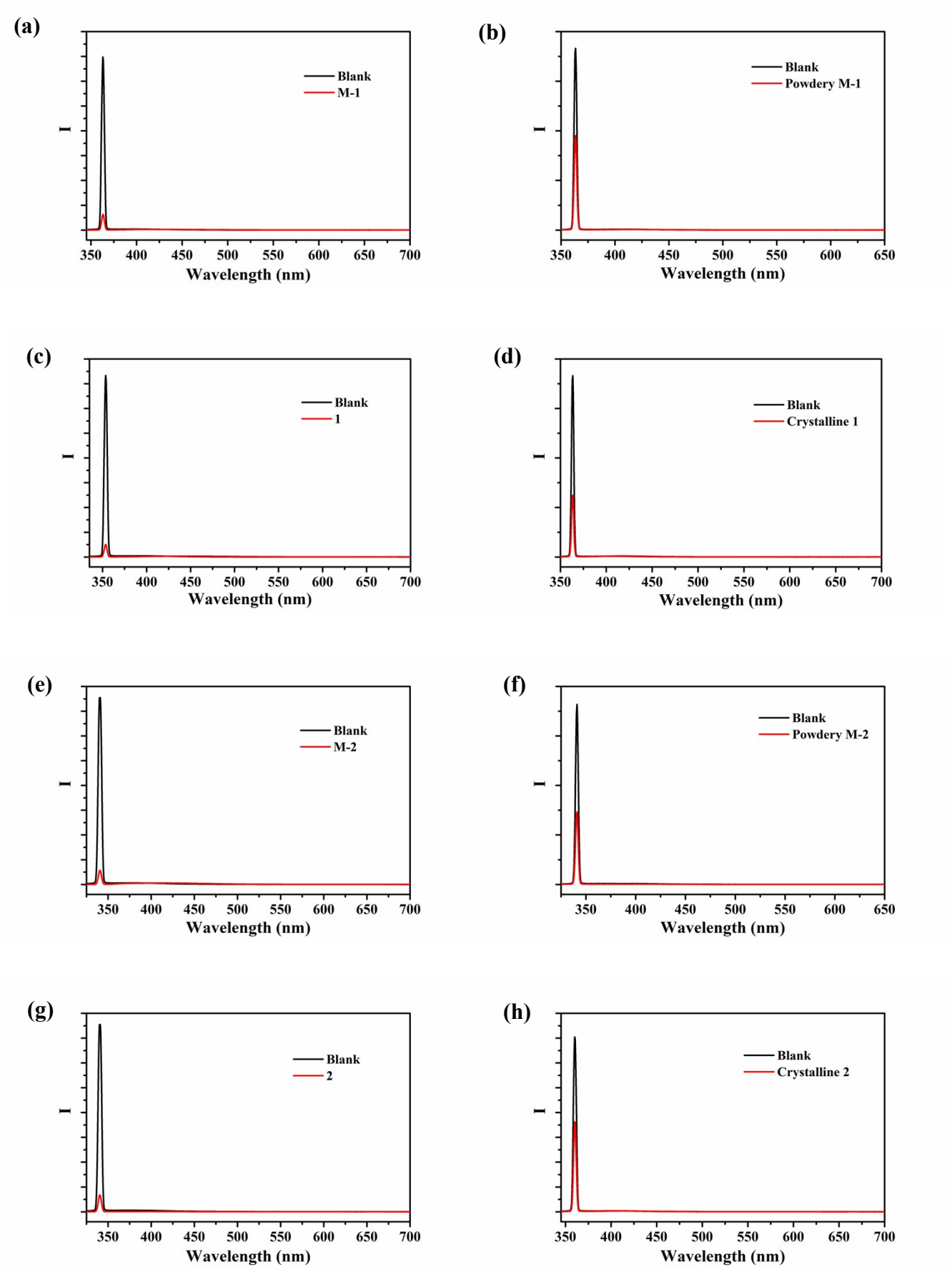
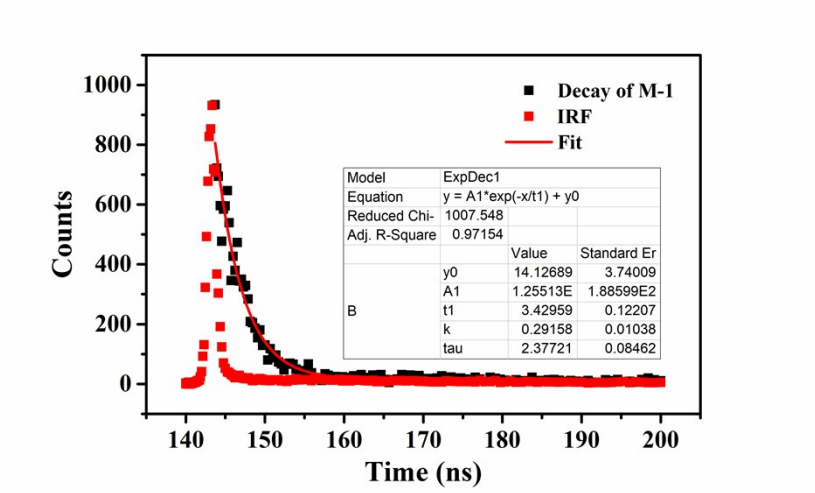

(a)
Blank
M-1
I
350 400 450 500 550 600 650 700
Wavelength (nm)
(b)
Blank
Powdery M-1
I
350 400 450 500 550 600 650
Wavelength (nm)
(c)
Blank
1
I
350 400 450 500 550 600 650 700
Wavelength (nm)
(d)
Blank
Crystalline 1
I
350 400 450 500 550 600 650 700
Wavelength (nm)
(e)
Blank
M-2
I
350 400 450 500 550 600 650 700
Wavelength (nm)
(f)
Blank
Powdery M-2
I
350 400 450 500 550 600 650
Wavelength (nm)
(g)
Blank
2
I
350 400 450 500 550 600 650 700
Wavelength (nm)
(h)
Blank
Crystalline 2
I
350 400 450 500 550 600 650 700
Wavelength (nm)

Table S4. Summary of the quantum yield

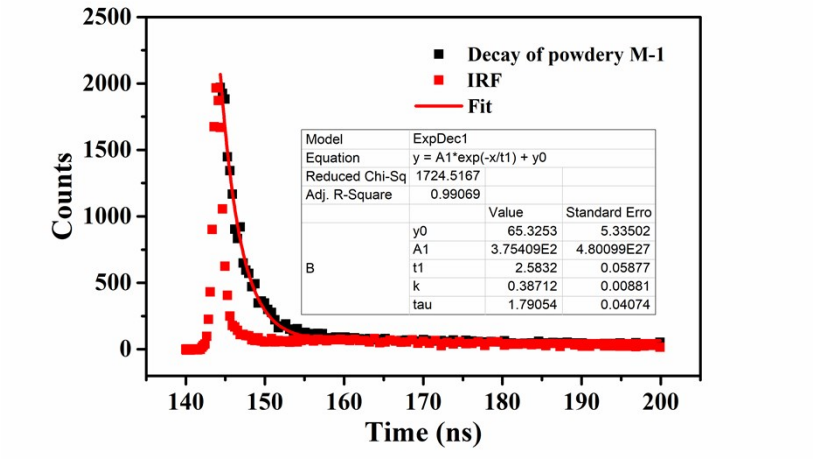
	λ_{ex}(nm)	λ_{em}(nm)	c(mM)	Φ_F	State
M-1	361	457	5	0.102	In acetonitrile
M-2	340	419	5	0.194	In acetonitrile
Powdery M-1	363	420	—	0.059	Powder
Powdery M-2	340	396	—	0.011	Powder
1	355	446	5	0.138	In acetonitrile
2	436	522	5	0.019	In acetonitrile
Crystalline 1	355	411	—	0.127	Crystal state
Crystalline 2	360	398	—	0.098	Crystal state

11. Figure S10. Emission decay curves.

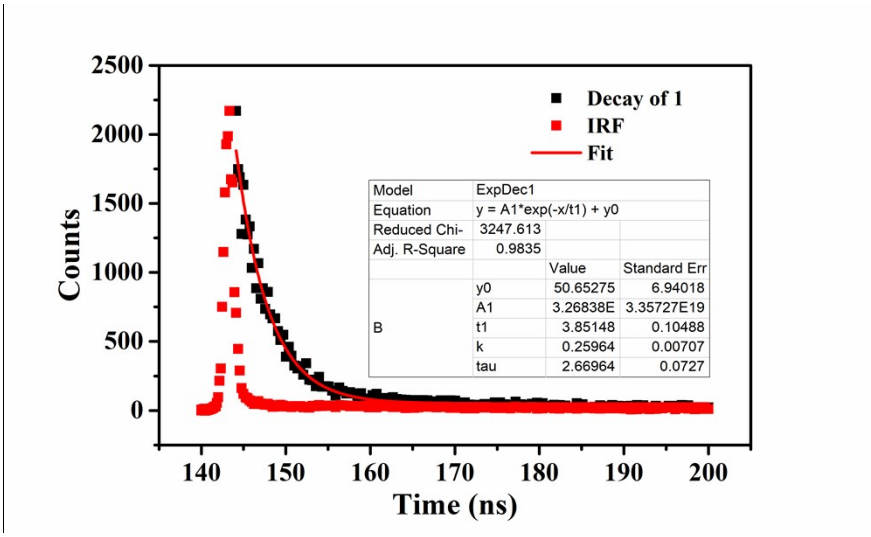
(a)



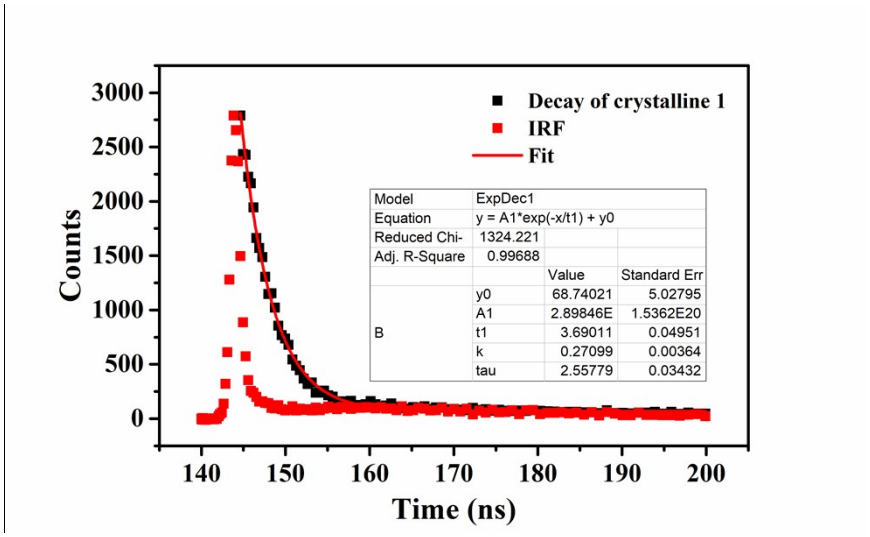
(b)



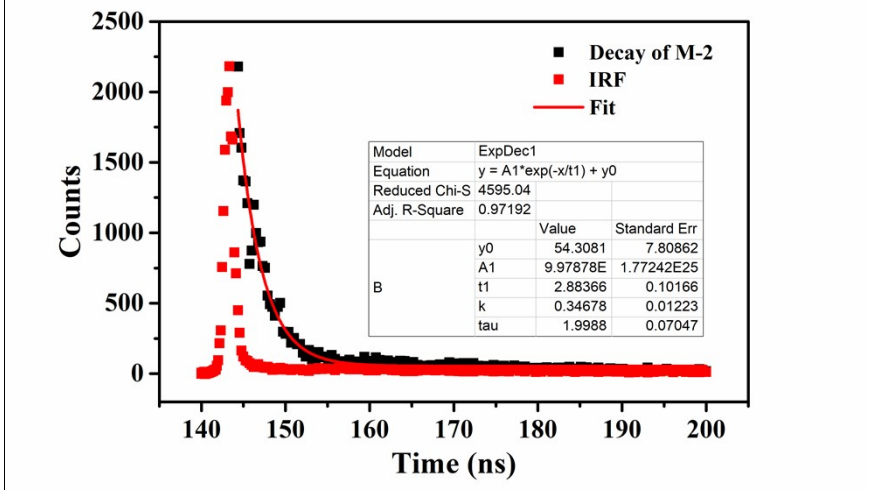
(c)


Decay of 1
IRF
Fit
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi- 3247.613
Adj. R-Square 0.9835
Value Standard Err
y0 50.65275 6.94018
A1 3.26838E 3.35727E19
B t1 3.85148 0.10488
k 0.25964 0.00707
tau 2.66964 0.0727
Counts
Time (ns)

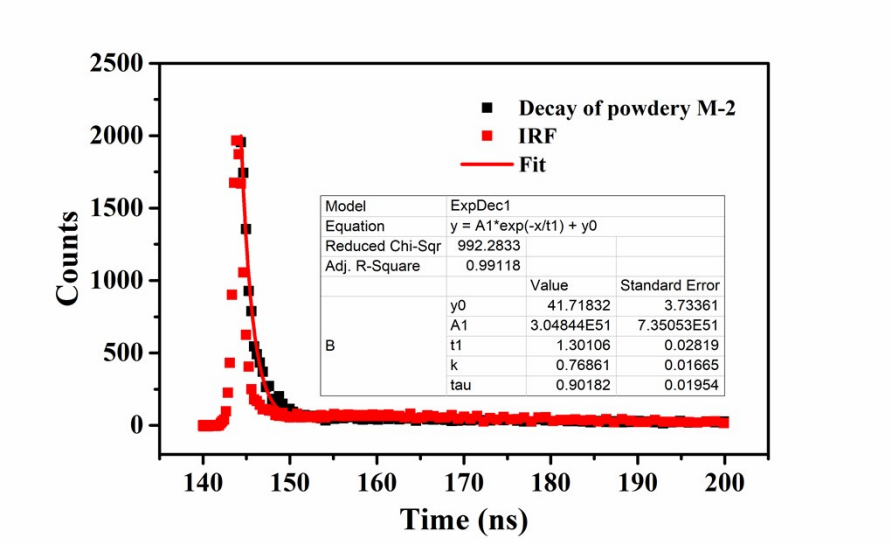
(d)


Decay of crystalline 1
IRF
Fit
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi- 1324.221
Adj. R-Square 0.99688
Value Standard Err
y0 68.74021 5.02795
A1 2.89846E 1.5362E20
B t1 3.69011 0.04951
k 0.27099 0.00364
tau 2.55779 0.03432
Counts
Time (ns)

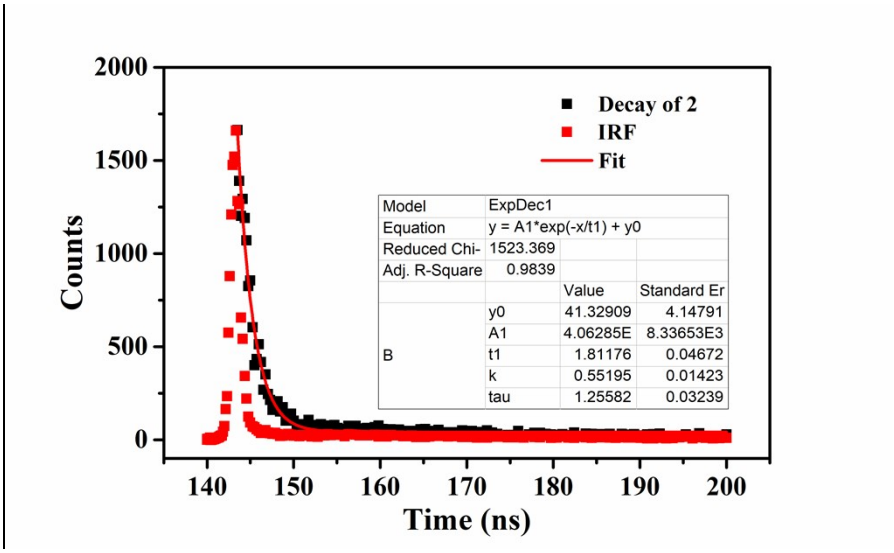
(e)


Decay of M-2
IRF
Fit
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-S 4595.04
Adj. R-Square 0.97192
Value Standard Err
y0 54.3081 7.80862
A1 9.97878E 1.77242E25
B t1 2.88366 0.10166
k 0.34678 0.01223
tau 1.9988 0.07047
Counts
Time (ns)

(f)


Decay of powdery M-2
IRF
Fit
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-Sqr 992.2833
Adj. R-Square 0.99118
Value Standard Error
B y0 41.71832 3.73361
A1 3.04844E51 7.35053E51
t1 1.30106 0.02819
k 0.76861 0.01665
tau 0.90182 0.01954
Counts
Time (ns)

(g)


Decay of 2
IRF
Fit
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi- 1523.369
Adj. R-Square 0.9839
Value Standard Er
B y0 41.32909 4.14791
A1 4.06285E 8.33653E3
t1 1.81176 0.04672
k 0.55195 0.01423
tau 1.25582 0.03239
Counts
Time (ns)

(h)

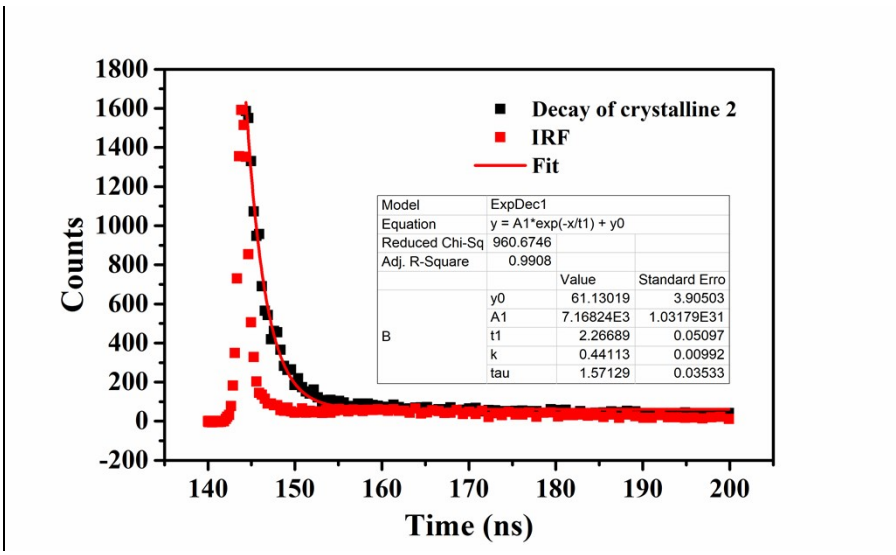

Decay of crystalline 2
IRF
Fit
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-Sq 960.6746
Adj. R-Square 0.9908
Value Standard Erro
B y0 61.13019 3.90503
A1 7.16824E3 1.03179E31
t1 2.26689 0.05097
k 0.44113 0.00992
tau 1.57129 0.03533
Counts
Time (ns)

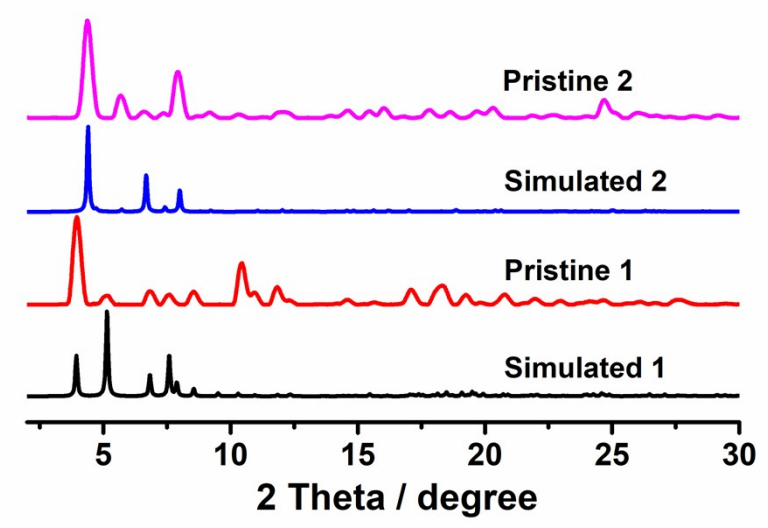
Table S5. Summary of the life time

	λ_{ex}(nm)	λ_{em}(nm)	c(mM)	(ns)	χ^2	State
M-1	**361**	**457**	**5**	**3.43**	**0.971**	**In acetonitrile**
M-2	**340**	**419**	**5**	**2.88**	**0.972**	**In acetonitrile**
Powdery M-1	**352**	**420**	**—**	**2.58**	**0.991**	**Powder**
Powdery M-2	**330**	**396**	**—**	**1.30**	**0.991**	**Powder**
1	**355**	**446**	**5**	**3.85**	**0.983**	**In acetonitrile**
2	**436**	**522**	**5**	**1.81**	**0.984**	**In acetonitrile**
Crystalline 1	**355**	**411**	**—**	**3.69**	**0.997**	**Crystal state**
Crystalline 2	**360**	**398**	**—**	**2.27**	**0.991**	**Crystal state**

12. Table S6. Summary of the optical properties of (*R*)-M-1, (*R*)-M-2, (*R*)-1, (*R*)-2, Crystalline (*R*)-1 and Crystalline (*R*)-2.

	λ_{max}(nm)	g_{CD}	λ_{em}(nm)	Stokes shift (nm)	Φ_F	(ns)	g_{lum}
(*R*)-M-1	**294**	**-6.9×10^{-4}**	**457**	**96**	**0.102**	**3.43**	**-1.2×10^{-3}**
(*R*)-M-2	**305**	**1.2×10^{-3}**	**419**	**79**	**0.194**	**2.88**	**1.4×10^{-3}**
Powdery (*R*)-M-1	**307**	**-2.7×10^{-4}**	**420**	**68**	**0.059**	**2.58**	**silent**
Powdery (*R*)-M-2	**308**	**5.1×10^{-4}**	**397**	**45**	**0.011**	**1.30**	**silent**
(*R*)-1	**304**	**-1.9×10^{-3}**	**446**	**91**	**0.138**	**3.85**	**-3.5×10^{-3}**
(*R*)-2	**294**	**3.8×10^{-3}**	**522**	**86**	**0.019**	**1.81**	**3.0×10^{-3}**
Crystalline (*R*)-1	**303**	**6.7×10^{-4}**	**411**	**56**	**0.127**	**3.69**	**2.6×10^{-3}**
Crystalline (*R*)-2	**311**	**2.9×10^{-4}**	**398**	**38**	**0.098**	**2.27**	**silent**

13. Figure S11. PXRD patterns.



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