Electronic Supporting Information for:

Photochromic Pyridylfulgenates and Their Cadmium Complexes

Ying-Ying Mai, Li Liu and Jing-Cao Dai*

Institute of Materials Physical Chemistry, Huaqiao University, Xiamen, Fujian 361021, China

* E-mail: djc@hqu.edu.cn

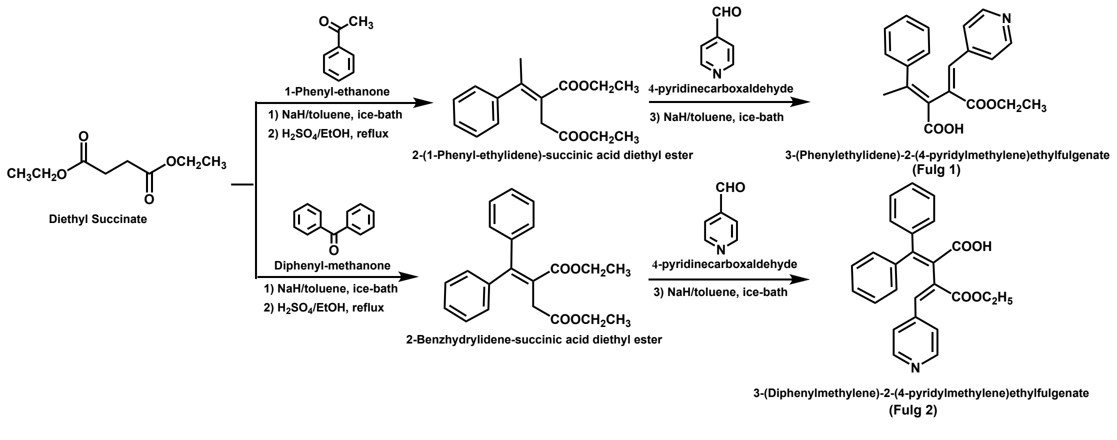
Content

1. Experimental Details

General Procedures. All chemicals for synthesis were of reagent grade quality purchased from commercial reagent companies, and used without further purification. ^{1}H and ^{13}C NMR spectra were conducted in Methanol-d$_4$ or DMSO-d$_6$ on a Bruker Avance III 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard in ppm. Infrared spectra were collected on a Thermo Scientific Nicolet iS50 spectrometer in the range of 4000-400 cm^{-1} using KBr plates. The C, H, and N elemental microanalyses were carried out with a Vario EL III elemental analyzer and the ESI-MS data were obtained from Agilent 8860-5977A mass spectrometry. Powder X-ray diffractions (PXRD) investigation were collected on polycrystalline samples in 2θ range of 3-50° using a Rigaku MinFlex600 diffractometer at 40 kV and 15 mA equipped with Cu Kα radiation (λ=1.5406Å) with a scan speed of 5°·min^{-1} and a step size of 0.02° in 2θ. Thermogravimetric analysis (TGA) were recorded on a Shimadzu DTG-60H instrument at a heating rate of 10 °C·min^{-1}. Photoirradiation was performed on a 300W AuLight Company model CEL-HXUV300 Xe lamp equipped with a monochromator at ambient temperature. The optical diffuse reflectance spectra were collected on a Shimadzu UV2550 spectrometer equipped with ISR-2200 integrating sphere using a pellet of barium sulfate as a 100% reference standard at room temperature. Fluorescent data were measured on an Edinburgh FL-FLS920 TCSPC system or an Edinburgh FL-FS5 fluorescence spectrophotometer.

1.1. Synthesis of Photochromic Pyridylfulgenates

The syntheses for all photochromic pyridylfulgenates are followed through two successive Stobbe condensations by a procedure as shown in Scheme S1.



Scheme S1 Synthetic route for photochromic pyridylfulgenates **Fulg1** and **Fulg2**.

1.1.1. 3-(phenylethylidene)-2-(4-pyridylmethylene)ethylfulgenate (Fulg1)

Diethyl succinate (98 % purity, 52.25 g, 294 mmol), absolute alcohol (2-3 drops) and phenyl ethanone (99 % purity, 36.03 g, 297 mmol) were successively added dropwise to a stirred suspension of sodium hydride (60 % purity, 12.04 g, 301 mmol) in 120 mL of toluene at ice-bath temperature. The reactants were then allowed to stir for reaction over 10 h followed by quenching of the reaction using a little distilled water (30 mL). After quenching of the reaction, the resulting product was extracted thrice by distilled water (3×80 mL) to remove the organic phase followed by the wash of aqueous phase with ethyl acetate twice (2×150 mL). The residual aqueous phase was acidified by concentrated hydrochloric acid (36 %) to reach a 2-3 of pH value for liberating the acid-ester. The liberated oil was extracted thrice again by appropriate ethyl acetate (3×50 mL) to remove the aqueous layer. The combined organic phases were dried by anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporator to give a dark brown oily syrup. The crude syrup was poured into petroleum ether (50 mL) and the mixture was allowed to stand for several hours to afford a precipitated solid followed separation by filtration. The filter residue was washed by a mixed solvent of dimethylbenzene-ethyl acetate-petroleum ether (v/v = 1:1:1) to provide 10.80 g (44 mmol, 15 % in yield) the half-ester intermediate of 2-(1-phenyl-ethylidene)-succinic acid-1-ethyl ester. This half-ester product (10.01 g, 40 mmol) was then dissolved in 40 mL absolute alcohol in a 100 mL round-bottom flask followed by the addition of 1 mL concentrated sulfuric acid (98 %) to reflux at 80 ℃ for 8-10 h for esterification. After esterification, alcohol solvent was removed by rotary evaporator, and the residue was added 30-50 mL of iced cold distilled water and then extracted thrice by diethyl ether (3×20 mL). Upon neutralization with a 10 % sodium carbonate aqueous solution, the combined organic phases were dried by anhydrous magnesium sulfate, and rotary evaporated to give a pale yellow liquid diester intermediate of 2-(1-phenyl-ethylidene)-succinic acid-diethyl ester (7.40 g, 27 mmol; 68 % in yield). Under a stirring condition, above 7.40 g of diester intermediate (27 mmol) was further dropped into an ice-cooled suspension of sodium hydride (0.80 g, 20 mmol) in 30 mL of toluene. Followed by addition of a few drops of absolute alcohol into the reaction mixture to initial the condensation reaction before dropwise addition of 4-pyridinecarboxaldehyde (2.14 g, 18 mmol). The reaction was allowed to keep up for 8-9 h and then quenched with a little distilled water. The resulting product was extracted twice by distilled water (2×30 mL) to remove the organic phase. The combined aqueous phases were washed thrice by appropriate ethyl acetate (3×30 mL) followed by addition of diluted hydrochloric acid to the basic solution to liberate the floccule oil. The liberated oil was extracted thrice again by ethyl acetate (3×50 mL) to remove the aqueous phase. The combined organic phases were dried by anhydrous magnesium sulfate, filtered, and removed the solvent by rotary evaporator to provide a crude product of 3-(phenylethylidene)-2-(4-pyridylmethylene)ethylfulgenate (Fulg1). Recrystallization of crude product from absolute alcohol was achieved by slow evaporation at room temperature for approximately 7 days to give the desired pure Fulg1 as colorless crystals (0.98 g, 3 mmol; 16 % in yield). ^{1}H NMR (500 MHz, Methanol-d_4): δ = 8.62 – 8.58 (m, 2H), 7.83 (s, 1H), 7.68 – 7.62 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.25 (m, 2H), 7.22 – 7.14 (m, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.76 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H) (see Figure S1); ^{13}C NMR (126 MHz, Methanol-d_4): δ = 169.89, 167.43, 151.14, 150.27, 145.20, 143.60, 139.25, 135.73, 128.98, 128.52, 127.42, 126.38, 124.92, 62.58, 24.03, 14.27 (Figure S2); HRMS (ESI, m/z): $[M]^+$ calcd for $C_{20}H_{18}NO_4$ 336.1236, found 336.1240 (Figure S3); IR (KBr pellet, cm^{-1}): v = 3414(w), 3077(w), 3020(w), 2996(m), 2986(m), 2935(w), 2906(w), 2444(m), 1945(m), 1715(vs), 1605(s), 1491(m), 1470(m), 1418(m), 1435(s), 1340(s), 1257(vs), 1135(s), 1069(s), 1014(s), 976(m), 934(m), 877(w), 827(s), 772(s), 761(s), 744(m), 699(s), 654(w), 608(s), 563(m), 525(m), 470(w) (Figure S4).

1.1.2. 3-(diphenylmethylene)-2-(4-pyridylmethylene)ethylfulgenate (Fulg2)

Similar to that for the preparation of Fulg1, a half-ester intermediate of 2-benzhydrylidene-succinic acid-1-ethyl ester (13.22 g, 43 mmol, yield 43 %) was obtained from substitution of phenyl ethanone by diphenyl methanone (18.21 g, 100 mmol) in the Stobbe condensation of diethyl succinate (98 % purity, 17.82 g, 100 mmol). Upon esterification with 0.5 mL concentrated sulfuric acid (98 %) and usual work-up, the pale yellow liquid of 2-benzhydrylidene-succinic acid diethyl ester (10.24 g, 30 mmol, yield 94 %) was obtained from above half-ester intermediate (10.0 g, 32 mmol) in 40 mL absolute alcohol. In a magnetic stirred suspension of sodium hydride (60 % purity, 1.12 g, 28 mmol) in 30 mL of toluene at ice-bath temperature, 10.24 g of above diethyl ester (30 mmol), 2 drops of absolute alcohol and 4-pyridinecarboxaldehyde (3.0 g, 25 mmol) were sequentially added dropwise off by an addition funnel. The reactants were allowed to react at room temperature for 24 h. After reaction completely, the resulting product was extracted by distilled water (50 mL) and separated to remove the organic layer. The aqueous phase was acidified to give rise to a faint yellow precipitate followed by filtration to receive a pale yellow powder of 3-(diphenylmethylene)-2-(4-pyridylmethylene)ethylfulgenate (Fulg2). The desired pure Fulg2 as the clear colorless crystals (6.53 g, 16 mmol; yield 65 %) was achieved by recrystallization of crude product from absolute alcohol. ^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 12.59 (s, 1H), 8.63 – 8.44 (m, 2H), 7.38 (s, 1H), 7.36 – 7.33 (m, 1H), 7.33 – 7.30 (m, 2H), 7.24 (m, 2H), 7.21 – 7.16 (m, 1H), 7.14 – 7.09 (m, 2H), 7.08 (m, 2H), 6.53 – 6.46 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H) (see Figure S5); ^{13}C NMR (126 MHz, Methanol-*d*$_4$): δ = 162.26, 158.53, 144.43, 140.52, 136.09, 133.47, 132.84, 130.64, 127.92, 121.04, 120.79, 120.14, 120.02, 119.67, 119.49, 118.11, 115.64, 53.42, 5.07 (see Figure S6); HRMS (ESI, m/z): [M·OH]$^-$ calcd for $C_{25}H_{21}NO_4{\cdot}OH^-$ 417.1537, found 417.1353 (Figure S7); IR (KBr pellet, cm^{-1}): 3416(w), 3052(w), 2975(w), 2935(w), 2709(w), 2513(m), 1950(m), 1720(vs), 1634(m), 1607(s), 1492(m), 1444(m), 1418(m), 1363(m), 1250(vs), 1212(vs), 1178(s), 1118(s), 1067(s), 1038(m), 1029(m), 1012(m), 906(w), 867(w), 856(w), 821(m), 767(s), 739(w), 702(s), 647(w), 620(w), 609(w), 584(m), 505(m) (Figure S8).

1.2. Synthesis of Cadmium-Fulgenate Frameworks

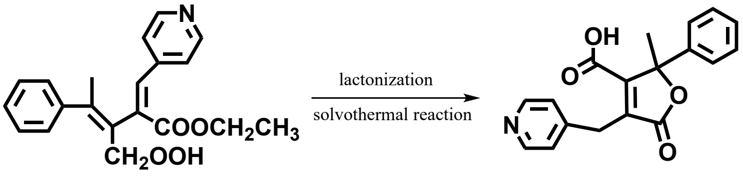
All the cadmium complexes were synthesized solvothermally in a 25 mL Parr Teflon-lined stainless steel autoclave under autogenous pressure.

1.2.1. [Cd$_2$(Fulg1)$_4$(DMF)]$_n$ (**1**)

The static reaction of $CdCl_2{\cdot}2.5H_2O$ (23 mg, 0.1 mmol), Fulg1 (34 mg, 0.1 mmol), DMF (3 mL) and H_2O (3 mL) was allowed to heat at 110 °C in a resistance furnace for 15 h followed by cooling at a rate of about 4 °C·h^{-1} to room temperature to give a about 11 % yield (18 mg) of **1** as colorless rodlike crystals, which were isolated by filtration and washed by both water and absolute alcohol. Its phase purity was supported by PXRD patterns (Figure S9). Anal. Calcd (found) for $C_{83}H_{79}N_5O_{17}Cd_2$ (**1**): C 60.66 (60.74), H 4.84 (4.84), N 4.26 (4.32). IR (KBr pellet, cm^{-1}): 3446(m), 3056(m), 2979(m), 2938(m), 2907(m), 1706(s), 1655(s), 1606(s), 1570(s), 1494(m), 1440(m), 1423(m), 1390(s), 1257(s), 1238(s), 1200(vs), 1146(m), 1100(m), 1072(m), 1036(m), 1012(m), 917(w), 831(m), 814(m), 766(m), 702(m), 677(w), 584(w), 550(w), 528(w) and 480(vw) (Figure S10).

1.2.2. [Cd(Fulg1’)(HCO$_2$)]$_n$ (**2**)

A mixture of Fulg1 (34 mg, 0.1 mmol) and NaOH (4 mg, 0.1 mmol) was dissolved in a DMF-MeOH-H_2O mixed solvent (6 mL, v/v = 1:2:3) in a 25 ml Parr Teflon-lined vial followed by addition of $CdCl_2{\cdot}2.5H_2O$ (46 mg, 0.2 mmol) under vigorous stirring to give a milky suspension. The reaction suspension was allowed to heat at 120 °C in a resistance furnace for 1 day followed by cooling at a rate of about 3 °C·h^{-1} to ambient temperature to reach an *in situ* ligand transformation (Scheme S2), providing a product of complex $[Cd(Fulg1')(HCO_2)]_n$ (**2**) (Fulg1' = 2-methyl-5-oxo-2-phenyl-4-(4-pyridylmethylene)-2,5-dihydrofuran-3-carboxylate) as colorless needle-like crystals (12 mg, yield 26 % based on Fulg1 source). Its phase purity has been approved by PXRD patterns (Figure S11). Anal. Calcd (found) for $C_{19}H_{15}NO_6Cd$ (**2**): C 48.95 (48.62), H 3.25 (3.13), N 3.01 (2.95). IR (KBr pellet, cm^{-1}): 3450(m), 3069(w), 2983(w), 2926(w), 2853(w), 2355(w), 1750(s), 1624(s), 1576(m), 1499(w), 1416(m), 1317(m), 1287(w), 1243(w), 1187(w), 1152(w), 1053(w), 1018(w), 919(w), 772(m), 711(w), 655(w) (Figure S12).



Fulg 1

Fulg 1'

Scheme S2 *in situ* ligand transformation of Fulg1' molecule

1.2.3. $[Cd(Fulg1')_2(H_2O)_2]_n$ (**3**)

Compound **3** was obtained as colorless needle-like crystals (22 mg, yield 29 % based on Fulg1 source) in a procedure similar to the preparation of **2** by a MeOH-H_2O mixed solvent (6 mL, v/v = 2:1) instead of above DMF-MeOH-H_2O solvent. Its phase purity has been approved by PXRD patterns (Figure S13). Anal. Calcd (found) for $C_{36}H_{32}N_2O_{10}Cd$ (**3**): C 56.47 (56.51), H 4.18 (3.90), N 3.66 (3.39). IR (KBr pellet, cm^{-1}): 3454(s), 3066(w), 2985(w), 2935(w), 1739(s), 1610(s), 1502(m), 1449(w), 1426(s), 1404(s), 1369(m), 1352(w), 1314(m), 1291(m), 1250(w), 1226(w), 1188(w), 1150(m), 1081(m), 1056(s), 1031(m), 930(m), 876(w), 784(m), 765(s), 697(s), 673 (w), 655(m), 586(w), 513(w), 483(w) (Figure S14).

1.2.4. $\{[Cd(Fulg2)_2(H_2O)]\cdot H_2O\}_n$ (**4**)

Synthesis of **4** was finished in a manner similar to that for the preparation of **1**. The static reaction of $CdCl_2\cdot 2.5H_2O$ (46 mg, 0.2 mmol), Fulg2 (40 mg, 0.1 mmol), and DMF-H_2O mixed solvent (6 mL, v/v = 1:1) was allowed to heat at 120 °C in a resistance furnace for 15 h followed by cooling at a rate of about 4 $°C\cdot h^{-1}$ to room temperature to give a about 23 % yield (22 mg, based on Fulg2 source) of **4** as colorless rodlike crystals, which were isolated by filtration and washed by both water and absolute alcohol. Its phase purity was supported by PXRD patterns (Figure S15). Anal. Calcd (found) for $C_{50}H_{44}N_2O_{10}Cd$ (**4**): C 63.53 (63.88), H 4.69 (4.64), N 2.96

(2.89). IR (KBr pellet, cm^{-1}): 3566(m), 3428(m), 3057(m), 2982(m), 2903(m), 1947(vw), 1714(vs), 1588(s), 1554(s), 1492(m), 1443(m), 1425(m), 1385(s), 1353(s), 1251(s), 1223(m), 1205(m), 1180(w), 1126(m), 1094(w), 1071(w), 1038(m), 927(w), 897(w), 884(w), 867(w), 853(w), 812(w), 798(w), 768(s), 698(s), 653(w), 607(w), 576(m), 491(w), 474(w) (Figure S16).

1.3. Structure Determinations

Single crystals with appropriate dimensions of 0.65×0.50×0.38 mm for Fulg1, 0.62×0.40×0.28 mm for Fulg2, 0.50×0.20×0.08 mm for **1**, 0.28×0.02×0.02 mm for **2**, 0.50×0.05×0.03 mm for **3**, and 0.90×0.30×0.20 mm for **4** were, respectively, selected with the aid of an optical microscope, then quickly coated with high vacuum grease and subsequently mounted on a fiber loop for single crystal X-ray data collection. Diffraction data were collected at 150 K with the aid of an Agilent Gemini/Xcalibur X-ray diffractometer equipped with monochromated Mo Kα radiation (λ = 0.71073 Å). The reflection intensities were reduced with the CryAlis^{Pro} software. The MUTI-SCAN program was applied on all of the data sets for empirical absorption corrections. The structures were solved by direct methods and refined by full-matrix least-squares techniques of F^2 using Shelxtl-2014 software package. All non-hydrogen atoms were treated anisotropically, and the organic hydrogen atoms were located in the riding model and treated isotropically. The Addsym subroutine PLATON was employed for checking these structures to ensure those models have no additional symmetry. Final refinements were converged at R_1 = 0.0532 for Fulg1, 0.0593 for Fulg2, 0.0713 for **1**, 0.0631 for **2**, 0.0422 for **3**, and 0.0446 for **4**, respectively. Some crystallographic data are given in Table S1. The important bond lengths and bond angles are presented in Table S2. The supplementary crystallographic information for these compounds have been deposited in the cif document as CCDC-2296151 for Fulg1, CCDC-2296035 for Fulg2, CCDC-2296038 for **1**, CCDC-1837617 for **2**, CCDC-1837618 for **3**, and CCDC-2296043 for **4**, respectively, which are available free of charge from the Cambridge Crystallographic Data Centre.

1.4. Theoretical Calculations

The electronic structures of both Fulg1 and Fulg2 molecules in crystal were evaluated by the density functional theory (DFT) and time-dependent density functional theory (TD–DFT) calculations, where employed the *Gaussian 16* program[S1] using B3LYP functional together with def2svp or def2tzvp basis set for all atom. Geometries were directly retrieved from the crystallographic data of either as the initial guess for further optimization, and all reported stationary points were verified as true minima by the absence of negative eigenvalues in the vibrational frequency analysis. The calculated spectra and molecular orbital analysis were using *Multiwfn 3.8(dev)* [S2] [S3].

TableS1. Crystal data collections and structure refinement parameters for Fulg1, Fulg2, and compounds **1-4**.

Compound	Fulg1(CCDC2296151)	Fulg2(CCDC2296035)	**1**(CCDC2296038)
empirical formula	$C_{20}H_{19}NO_4$	$C_{25}H_{21}NO_4$	$C_{83}H_{79}N_5O_{17}Cd_2$
formula weight	337.36	399.43	1643.31
T (°K)	293(2)	293(2)	293(2)
λ (Å)	0.71073 (Mo–$K\alpha$)	0.71073 (Mo–$K\alpha$)	0.71073 (Mo–$K\alpha$)
Crystal system, Space group, Z	Orthorhombic, $P\mathrm{na}2_1$, 4	Monoclinic, $P2_1$/c, 8	Monoclinic, $P2_1$/c, 4
a, b, c (Å)	12.581(1), 9.866(1), 14.738(1)	16.1979(7), 22.8193(8), 11.8386(5)	16.412(1),17.230(2), 28.202(2)
α, β, γ (°)	90, 90, 90	90, 100.545(4), 90	90, 92.706(6), 90
V (Å^3)	1829.3(3)	4301.9(3)	7966(1)
ρ_{calcd} (g·cm^3)	1.225	1.233	1.370
μ (mm^{-1})	0.086	0.084	0.603
F(000)	712	1680	3376
Crystal size (mm)	0.66×0.50×0.38	0.62×0.40×0.28	0.50×0.20×0.08
θ Range (°)	3.5 – 25.0	3.5 – 25.0	3.4 – 25.0
Collected reflections	4772	18918	36753
Unique reflections	2719	7548	13947
Observed reflections	1877	4710	9294
R_{int}	0.0333	0.0319	0.0566
Data / restraints / parameters	2719 / 1 / 226	7548 / 12 / 542	13947 / 145 / 952
GOF	0.999	1.016	1.025
R indices (for obs.):			
R_1 ^{a}, wR_2^{b}	0.0532, 0.1205	0.0593, 0.1449	0.0713, 0.1607
R indices (for all):			
R_1, wR_2	0.0895, 0.1413	0.1018, 0.1770	0.1124, 0.1865
Largest diff. peak/hole (e.Å^{-3})	0.20/ -0.16	0.25/ -0.30	1.39/ -1.00

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

(continued)

Compound	**2**(CCDC1837617)	**3**(CCDC1837618)	**4**(CCDC2296043)
empirical formula	$C_{19}H_{15}NO_6Cd$	$C_{36}H_{32}N_2O_{10}Cd$	$C_{50}H_{44}N_2O_{10}Cd$
formula weight	465.72	765.03	945.27
T (°K)	293(2)	293(2)	293(2)
λ (Å)	0.71073 (Mo–$K\alpha$)	0.71073 (Mo–$K\alpha$)	0.71073 (Mo–$K\alpha$)
Crystal system, Space group, Z	Trigonal, $R\bar{3}$, 18	Monoclinic, $P2_1$/n, 2	Monoclinic, $P2_1$/c, 4
a, b, c (Å)	33.209(2), 33.209(2), 8.3584(9)	12.142(1), 8.5142(7), 16.483(1)	17.4412(5),14.5878(4),17.9857(5)
α, β, γ (°)	90, 90, 120	90, 96.129(7), 90	90, 107.952(3), 90
V (Å^3)	7983(1)	1694.3(2)	4353.3(2)
ρ_{calcd} (g·cm^3)	1.744	1.500	1.442
μ (mm^{-1})	1.268	0.706	0.565
F(000)	4176	780	1944
Crystal size (mm)	0.28×0.02×0.02	0.50×0.05×0.03	0.90×0.30×0.20
θ Range (°)	2.8 – 25.5	2.9 – 25.0	3.4 – 26.0
Collected reflections	9016	6934	19799
Unique reflections	3297	2961	8523
Observed reflections	2029	2302	6474
R_{int}	0.0892	0.0283	0.0437
Data / restraints / parameters	3297 / 0 / 245	2961 / 12 / 219	8523 / 4 / 568
GOF	1.002	1.079	1.021
R indices (for obs.):			
R_1 ^{a}, wR_2^{b}	0.0631, 0.1022	0.0422, 0.0993	0.0446, 0.0881
R indices (for all):			
R_1, wR_2	0.1223, 0.1260	0.0586, 0.1090	0.0658, 0.0956
Largest diff. peak/hole (e.Å^{-3})	0.98/ -0.74	1.18/ -0.80	0.72/ -0.72

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

Table S2. Selected geometrical parameters for Fulg1, Fulg2, and compounds **1-4** [Å and °].

Fulg1			
Bond lengths			
O(3)-C(6)	1.198(6)	C(2)-C(6)	1.489(7)
O(4)-C(6)	1.295(6)	C(3)-C(4)	1.335(6)
C(1)-C(2)	1.323(6)	C(3)-C(5)	1.490(6)
C(2)-C(3)	1.507(6)		
Bond angles			
C(1)-C(2)-C(3)	127.7(4)	C(3)-C(2)-C(6)	112.6(4)
C(1)-C(2)-C(6)	119.7(4)	C(3)-C(4)-C(20)	123.8(4)
C(2)-C(1)-C(11)	128.4(4)	C(3)-C(4)-C(14)	122.2(4)
C(2)-C(3)-C(4)	121.5(4)	C(4)-C(3)-C(5)	123.9(4)
C(2)-C(3)-C(5)	114.5(4)	C(14)-C(4)-C(20)	114.0(5)
Torsion angles			
C(1)-C(2)-C(3)-C(4)	74.7		
Hydrogen bonds[i]			

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(02)...N(*a*)	0.85	1.802	2.6567(2)	174.5

Fulg2			
Bond lengths			
C(1)-C(2)	1.327(3)	C(31)-C(32)	1.332(3)
C(2)-C(3)	1.481(3)	C(32)-C(33)	1.485(3)
C(2)-C(6)	1.496(4)	C(32)-C(36)	1.490(3)
C(3)-C(4)	1.347(3)	C(33)-C(34)	1.347(3)
C(3)-C(5)	1.505(3)	C(33)-C(35)	1.501(3)
Bond angles			
C(1)-C(2)-C(3)	125.4(2)	C(31)-C(32)-C(33)	125.1(2)
C(1)-C(2)-C(6)	115.7(2)	C(31)-C(32)-C(36)	116.9(2)
C(2)-C(1)-C(11)	127.2(2)	C(32)-C(31)-C(41)	125.8(2)
C(2)-C(3)-C(4)	125.6(2)	C(32)-C(33)-C(34)	122.7(2)
C(2)-C(3)-C(5)	115.4(2)	C(32)-C(33)-C(35)	116.4(2)
C(3)-C(2)-C(6)	118.9(2)	C(33)-C(32)-C(36)	118.0(2)
C(3)-C(4)-C(14)	123.4(2)	C(33)-C(34)-C(44)	122.7(2)
C(3)-C(4)-C(20)	121.6(2)	C(33)-C(34)-C(50)	122.8(2)
C(4)-C(3)-C(5)	119.0(2)	C(34)-C(33)-C(35)	120.9(2)
C(14)-C(4)-C(20)	115.0(2)	C(44)-C(34)-C(50)	114.4(2)
Torsion angles			
C(1)-C(2)-C(3)-C(4)	56.3	C(31)-C(32)-C(33)-C(34)	60.1
Hydrogen bonds[ii]			

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(02)...N(2*a*)	0.87	1.821	2.6580(1)	161.6
O(6*b*)-H(06*b*)...N(1)	0.87	1.812	2.6763(1)	175.0

1[a]			
Bond lengths			

Cd(1)-N(1)	2.402(6)	Cd(2)-N(2b)	2.297(6)
Cd(1)-N(3)	2.374(5)	Cd(2)-N(4c)	2.334(6)
Cd(1)-O(01)	2.439(6)	Cd(2)-O(1)	2.457(5)
Cd(1)-O(5)	2.383(5)	Cd(2)-O(2)	2.269(5)
Cd(1)-O(6)	2.379(5)	Cd(2)-O(9a)	2.298(5)
Cd(1)-O(13)	2.335(6)	Cd(2)-O(10a)	2.428(5)
Cd(1)-O(14)	2.495(6)	O(01)-C(01)	1.22(1)
O(3)-C(6)	1.176(9)	O(11)-C(46)	1.22(1)
O(4)-C(6)	1.34(1)	O(12)-C(46)	1.333(9)
C(1)-C(2)	1.36(1)	C(41)-C(42)	1.34(1)
C(2)-C(3)	1.467(9)	C(42)-C(43)	1.49(1)
C(2)-C(6)	1.49(1)	C(42)-C(46)	1.48(1)
C(3)-C(4)	1.35(1)	C(43)-C(44)	1.33(1)
C(3)-C(5)	1.502(9)	C(43)-C(45)	1.503(9)
C(21)-C(22)	1.32(1)	C(61)-C(62)	1.316(9)
C(22)-C(23)	1.504(9)	C(62)-C(63)	1.506(9)
C(22)-C(26)	1.49(1)	C(62)-C(66)	1.50(1)
C(23)-C(24)	1.333(9)	C(63)-C(64)	1.32(1)
C(23)-C(25)	1.524(9)	C(63)-C(65)	1.52(1)
Bond angles			
N(1)-Cd(1)-N(3)	94.9(2)	O(14)-Cd(1)-O(01)	90.3(2)
O(5)-Cd(1)-N(1)	86.5(2)	O(01)-Cd(1)-N(1)	174.6(2)
O(5)-Cd(1)-N(3)	80.3(2)	O(01)-Cd(1)-N(3)	81.0(2)
O(5)-Cd(1)-O(6)	54.9(2)	N(2*b*)-Cd(2)-N(4*c*)	98.0(2)
O(5)-Cd(1)-O(13)	145.4(2)	O(1)-Cd(2)-N(2*b*)	87.3(2)
O(5)-Cd(1)-O(14)	162.4(2)	O(1)-Cd(2)-N(4*c*)	84.2(2)
O(5)-Cd(1)-O(01)	89.4(2)	O(1)-Cd(2)-O(2)	54.9(2)
O(6)-Cd(1)-N(1)	97.7(2)	O(1)-Cd(2)-O(9*a*)	143.2(2)
O(6)-Cd(1)-N(3)	132.3(2)	O(1)-Cd(2)-O(10*a*)	150.2(2)
O(6)-Cd(1)-O(13)	91.5(2)	O(2)-Cd(2)-N(2*b*)	110.1(2)
O(6)-Cd(1)-O(14)	142.4(2)	O(2)-Cd(2)-N(4*c*)	127.3(2)
O(6)-Cd(1)-O(01)	82.7(2)	O(2)-Cd(2)-O(9*a*)	108.9(2)
O(13)-Cd(1)-N(1)	90.9(2)	O(2)-Cd(2)-O(10*a*)	100.9(2)
O(13)-Cd(1)-N(3)	134.2(2)	O(9*a*)-Cd(2)-N(2*b*)	128.7(2)
O(13)-Cd(1)-O(14)	52.1(2)	O(9*a*)-Cd(2)-N(4*c*)	83.4(2)
O(13)-Cd(1)-O(01)	94.5(2)	O(9*a*)-Cd(2)-O(10*a*)	55.2(2)
O(14)-Cd(1)-N(1)	92.6(2)	O(10*a*)-Cd(2)-N(2*b*)	85.7(2)
O(14)-Cd(1)-N(3)	82.2(2)	O(10*a*)-Cd(2)-N(4*c*)	125.5(2)
C(1)-C(2)-C(3)	125.2(6)	C(41)-C(42)-C(43)	126.0(6)
C(1)-C(2)-C(6)	115.5(7)	C(41)-C(42)-C(46)	117.2(7)
C(2)-C(1)-C(11)	128.8(7)	C(42)-C(41)-C(51)	127.8(7)
C(2)-C(3)-C(4)	124.6(6)	C(42)-C(43)-C(44)	122.3(6)
C(2)-C(3)-C(5)	115.5(6)	C(42)-C(43)-C(45)	112.7(6)

C(3)-C(2)-C(6)	119.2(7)	C(43)-C(42)-C(46)	116.7(6)
C(3)-C(4)-C(14)	120.7(6)	C(43)-C(44)-C(54)	123.1(6)
C(3)-C(4)-C(20)	123.4(7)	C(43)-C(44)-C(60)	120.4(7)
C(4)-C(3)-C(5)	119.8(6)	C(44)-C(43)-C(45)	124.9(7)
C(14)-C(4)-C(20)	115.9(7)	C(54)-C(44)-C(60)	116.4(7)
C(21)-C(22)-C(23)	123.5(7)	C(61)-C(62)-C(63)	125.4(6)
C(21)-C(22)-C(26)	120.4(7)	C(61)-C(62)-C(66)	115.9(7)
C(22)-C(21)-C(31)	126.0(7)	C(62)-C(61)-C(71)	129.1(7)
C(22)-C(23)-C(24)	122.6(6)	C(62)-C(63)-C(64)	124.4(6)
C(22)-C(23)-C(25)	114.3(6)	C(62)-C(63)-C(65)	110.8(7)
C(23)-C(22)-C(26)	116.1(6)	C(63)-C(62)-C(66)	118.6(6)
C(23)-C(24)-C(34)	124.0(6)	C(63)-C(64)-C(74)	122.1(6)
C(23)-C(24)-C(40)	121.2(7)	C(63)-C(64)-C(80)	124.5(7)
C(24)-C(23)-C(25)	123.2(6)	C(64)-C(63)-C(65)	124.5(7)
C(34)-C(24)-C(40)	114.7(7)	C(74)-C(64)-C(80)	113.4(7)
Torsion angles			
C(1)-C(2)-C(3)-C(4)	63.5	C(41)-C(42)-C(43)-C(44)	87.6
C(21)-C(22)-C(23)-C(24)	71.4	C(61)-C(62)-C(63)-C(64)	65.2
2[b]			
Bond lengths			
Cd-O(1)	2.240(5)	O(4)-C(4)	1.472(8)
Cd-O(2*a*)	2.268(5)	O(4)-C(6)	1.340(9)
Cd-O(6*b*)	2.279(5)	C(1)-C(2)	1.501(9)
Cd-O(6*d*)	2.317(5)	C(2)-C(3)	1.335(9)
Cd-O(5)	2.339(5)	C(2)-C(6)	1.47(1)
Cd-N(*c*)	2.308(6)	C(3)-C(4)	1.51(1)
O(3)-C(6)	1.197(8)	C(3)-C(5)	1.49(1)
Bond angles			
O(1)-Cd-O(2*a*)	87.1(2)	O(6*d*)-Cd-N(*c*)	97.2(2)
O(1)-Cd-O(5)	173.0(2)	C(2)-C(3)-C(4)	109.5(7)
O(1)-Cd-O(6*b*)	95.7(2)	C(2)-C(6)-O(4)	108.7(7)
O(1)-Cd-O(6*d*)	94.9(2)	C(3)-C(4)-O(4)	102.5(6)
O(1)-Cd-N(*c*)	90.1(2)	C(3)-C(2)-C(6)	108.8(7)
O(5)-Cd-O(2*a*)	95.2(2)	C(4)-O(4)-C(6)	110.4(6)
O(5)-Cd-O(6*b*)	91.2(2)	C(1)-C(2)-C(3)	129.8(7)
O(5)-Cd-O(6*d*)	83.5(2)	C(1)-C(2)-C(6)	121.3(7)
O(5)-Cd-N(*c*)	83.3(2)	C(2)-C(1)-C(11)	112.0(6)
O(2*a*)-Cd-O(6*b*)	84.5(2)	C(2)-C(3)-C(5)	127.3(7)
O(2*a*)-Cd-O(6*d*)	173.7(2)	C(3)-C(4)-C(14)	113.4(6)
O(2*a*)-Cd-N(*c*)	88.7(2)	C(3)-C(4)-C(20)	112.0(6)
O(6*b*)-Cd-O(6*d*)	89.4(2)	C(4)-C(3)-C(5)	123.2(7)
O(6*b*)-Cd-N(*c*)	170.8(2)	C(14)-C(4)-C(20)	114.8(7)
Torsion angles			

C(1)-C(2)-C(3)-C(4)	179.0		
3[c]			
Bond lengths			
Cd-O(1)	2.258(3)	C(1)-C(2)	1.507(6)
Cd-O(5)	2.347(3)	C(2)-C(3)	1.322(5)
Cd-N(*b*)	2.342(3)	C(2)-C(6)	1.475(5)
O(3)-C(6)	1.198(5)	C(3)-C(4)	1.522(5)
O(4)-C(4)	1.476(5)	C(3)-C(5)	1.516(5)
O(4)-C(6)	1.342(5)		
Bond angles			
O(1)-Cd-O(1*a*)	180.0	C(3)-C(2)-C(6)	107.9(4)
O(5)-Cd-O(5*a*)	180.0	C(3)-C(4)-O(4)	101.8(3)
N(*b*)-Cd-N(*c*)	180.0	C(4)-O(4)-C(6)	110.2(3)
O(1)-Cd-O(5)	89.3(1)	C(1)-C(2)-C(3)	131.2(4)
O(1)-Cd-O(5*a*)	90.7(1)	C(1)-C(2)-C(6)	120.8(4)
O(1)-Cd-N(*b*)	89.3(1)	C(2)-C(1)-C(11)	113.3(4)
O(1)-Cd-N(*c*)	90.7(1)	C(2)-C(3)-C(5)	127.2(4)
O(5)-Cd-N(*b*)	89.1(1)	C(4)-C(3)-C(5)	122.2(4)
O(5)-Cd-N(*c*)	90.9(1)	C(3)-C(4)-C(14)	112.4(3)
C(2)-C(3)-C(4)	110.6(3)	C(3)-C(4)-C(20)	112.8(3)
C(2)-C(6)-O(4)	109.4(3)	C(14)-C(4)-C(20)	114.7(4)
Torsion angles			
C(1)-C(2)-C(3)-C(4)	177.7		
4[d]			
Bond lengths			
Cd-O(1)	2.240(2)	Cd-O(5)	2.416(2)
Cd-O(01)	2.349(2)	Cd-O(6)	2.332(2)
Cd-N(1)	2.287(3)	Cd-N(2)	2.337(2)
C(1)-C(2)	1.335(4)	C(31)-C(32)	1.333(4)
C(2)-C(3)	1.488(4)	C(32)-C(33)	1.494(4)
C(3)-C(4)	1.346(4)	C(33)-C(34)	1.347(4)
C(3)-C(5)	1.507(4)	C(33)-C(35)	1.504(4)
C(2)-C(6)	1.495(4)	C(32)-C(36)	1.489(4)
Bond angles			
O(1)-Cd-O(5)	168.42(7)	C(2)-C(3)-C(5)	114.8(2)
O(1)-Cd-O(6)	117.17(8)	C(4)-C(3)-C(5)	121.5(3)
O(1)-Cd-O(01)	89.25(8)	C(3)-C(4)-C(14)	121.6(3)
O(5)-Cd-O(6)	54.98(7)	C(3)-C(4)-C(20)	122.1(3)
O(5)-Cd-O(01)	97.09(8)	C(1)-C(2)-C(6)	115.7(3)
O(6)-Cd-O(01)	80.12(8)	C(3)-C(2)-C(6)	119.6(3)
N(1)-Cd-N(2)	96.70(9)	C(14)-C(4)-C(20)	116.3(2)
N(1)-Cd-O(1)	98.51(9)	C(31)-C(32)-C(33)	124.0(3)
N(1)-Cd-O(5)	91.47(8)	C(32)-C(33)-C(34)	121.0(3)

N(1)-Cd-O(6)	141.73(9)	C(32)-C(31)-C(41*c*)	126.1(3)
N(1)-Cd-O(01)	87.41(9)	C(32)-C(33)-C(35)	115.1(3)
N(2)-Cd-O(1)	85.37(8)	C(34)-C(33)-C(35)	123.8(3)
N(2)-Cd-O(5)	87.66(8)	C(33)-C(34)-C(44)	123.2(3)
N(2)-Cd-O(6)	99.36(8)	C(33)-C(34)-C(50)	121.4(3)
N(2)-Cd-O(01)	173.66(9)	C(31)-C(32)-C(36)	120.8(3)
C(1)-C(2)-C(3)	124.5(3)	C(33)-C(32)-C(36)	115.1(3)
C(2)-C(3)-C(4)	123.6(3)	C(44)-C(34)-C(50)	115.3(3)
C(2)-C(1)-C(11*a*)	125.0(3)		
Torsion angles			
C(1)-C(2)-C(3)-C(4)	60.5	C(31)-C(32)-C(33)-C(34)	61.9

Symmetry code:

[i] *a*= 3/2-x,-1/2+y,-1/2+z. [ii] *a* = -1-x,1-y,-z; *b* = -x,1-y,-z. [a] *a* = -x,y+1/2,-z+1/2; *b* = x,y+1,z; *c* = -x+1,y+1/2,-z+1/2. [b] *a* = x-y,x,-z+1; *b* = y,-x+y,-z+1; *c* = x,y,z+1; *d* = -x+y,-x,z. [c] *a* =-x+1,-y,-z+1; *b* = -x+1,-y+1,-z+1; *c* = x,y-1,z. [d] *a* = -x-1,y+1/2,-z-1/2; *c* = x,-y+3/2,z-1/2.

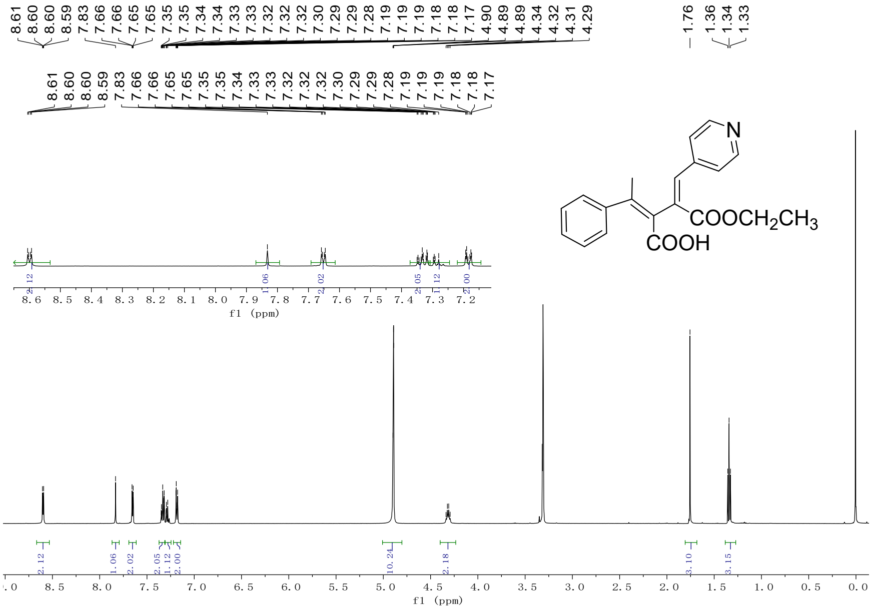


Figure S1. ^{1}H NMR Spectrum of Fulg 1.

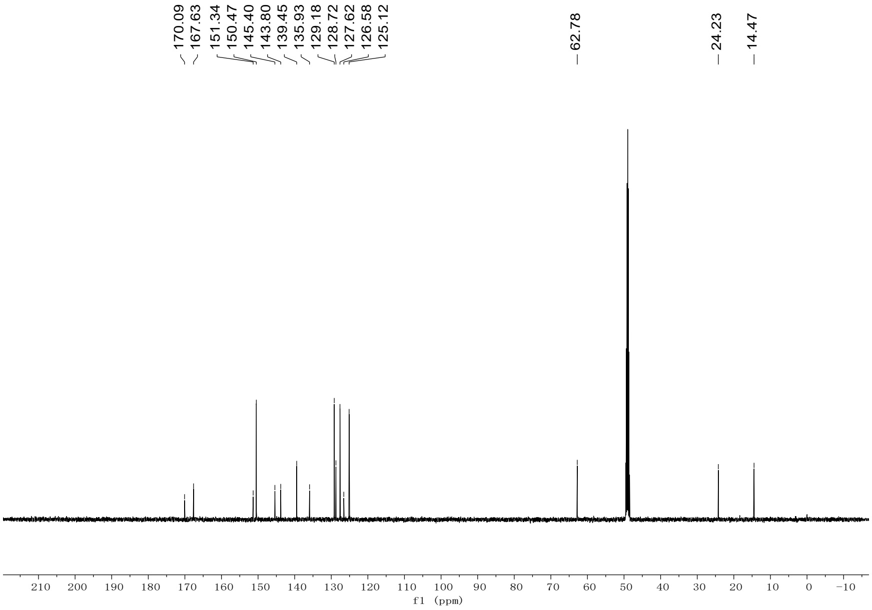


Figure S2. ^{13}C NMR Spectrum of Fulg 1.

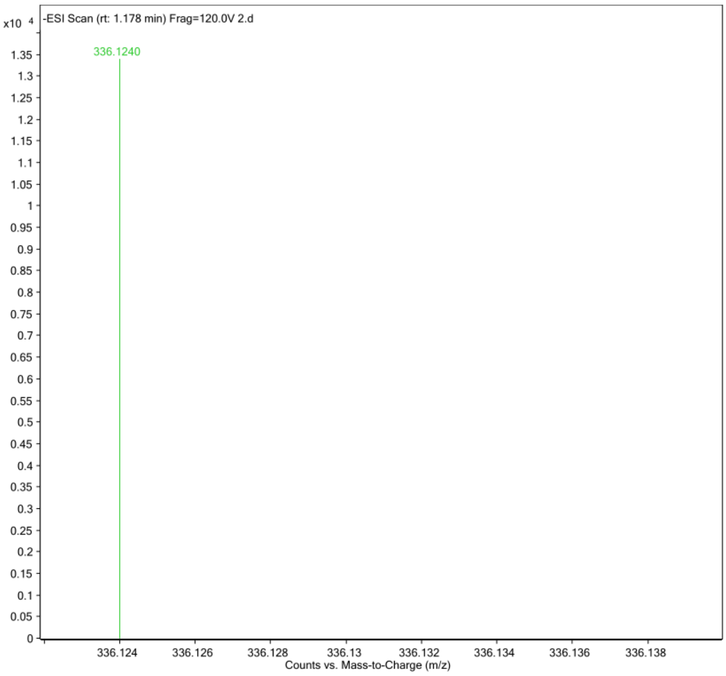


Figure S3. HRMS(ESI) data of Fulg 1.

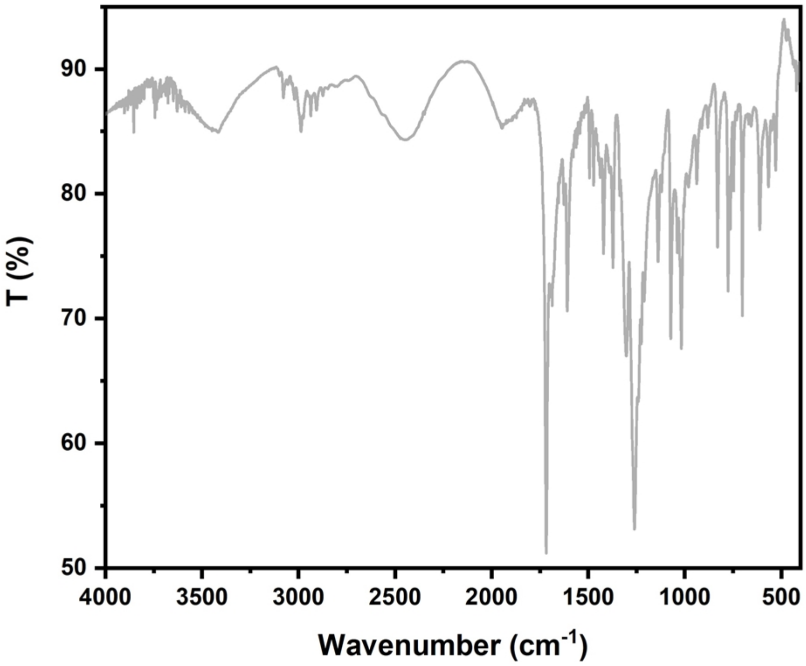


Figure S4. FT-IR spectra of Fulg 1.

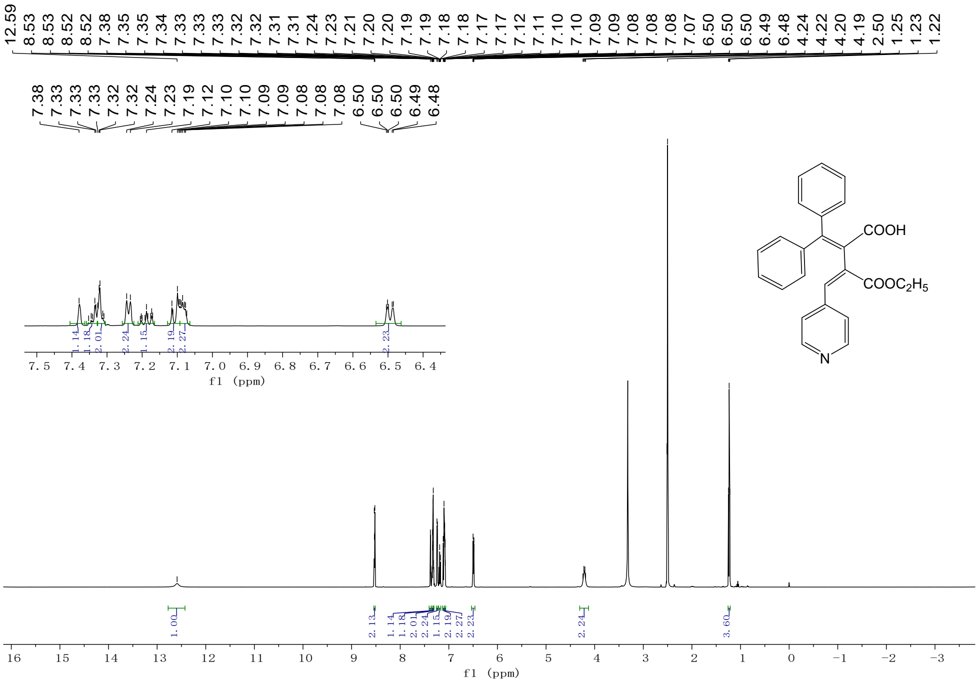


Figure S5. ^{1}H NMR Spectrum of Fulg 2.

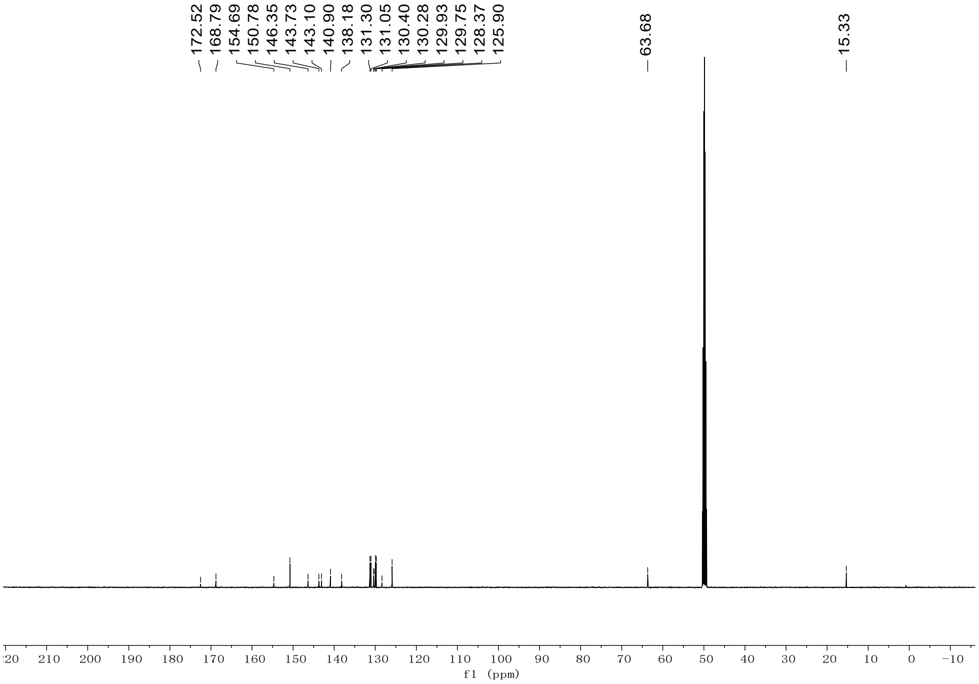


Figure S6. ^{13}C NMR Spectrum of Fulg 2.

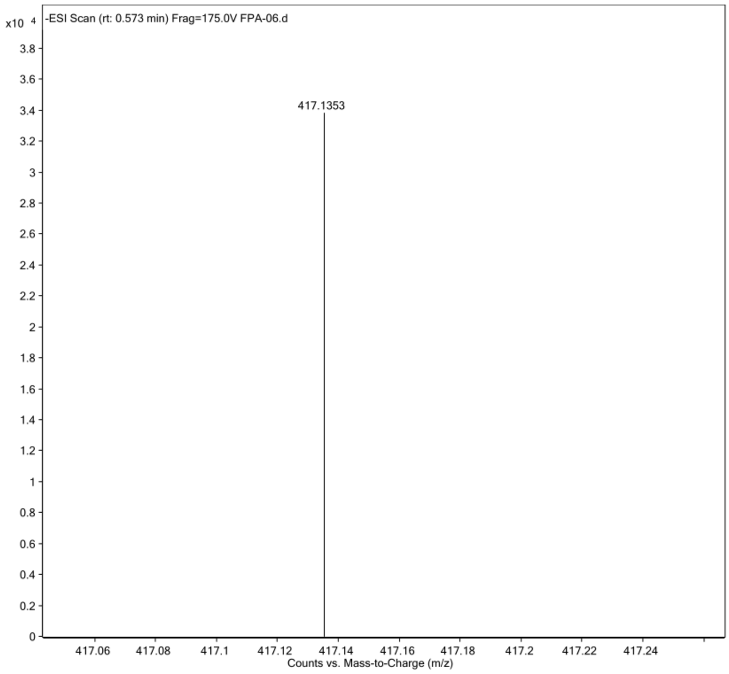


Figure S7. HRMS(ESI) data of Fulg 2.

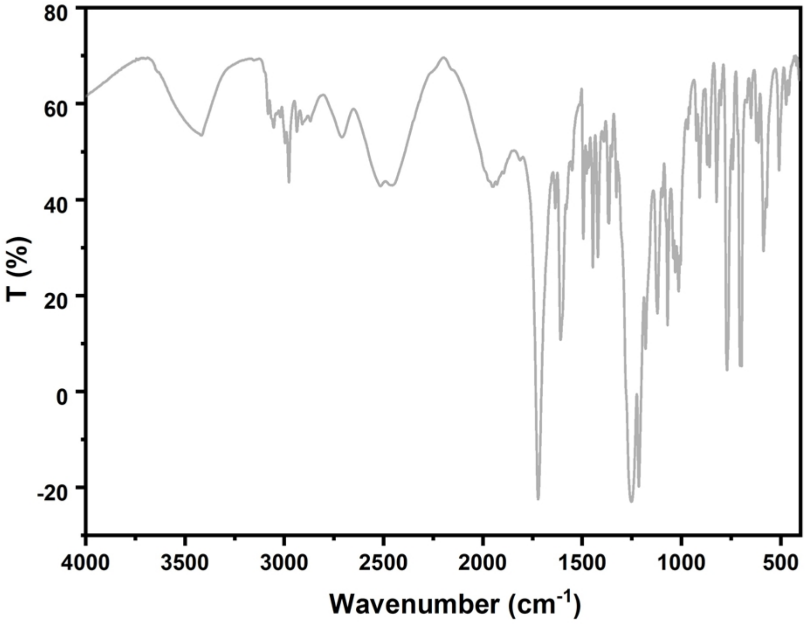


Figure S8. FT-IR spectra of Fulg 2.

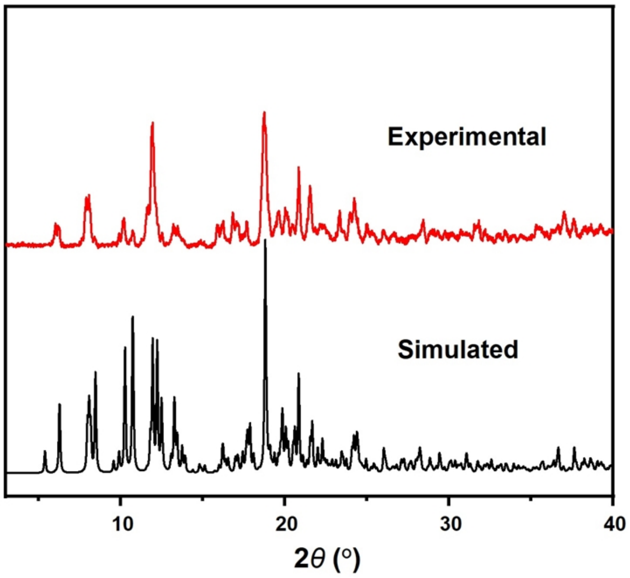


Figure S9. PXRD patterns of **1**.

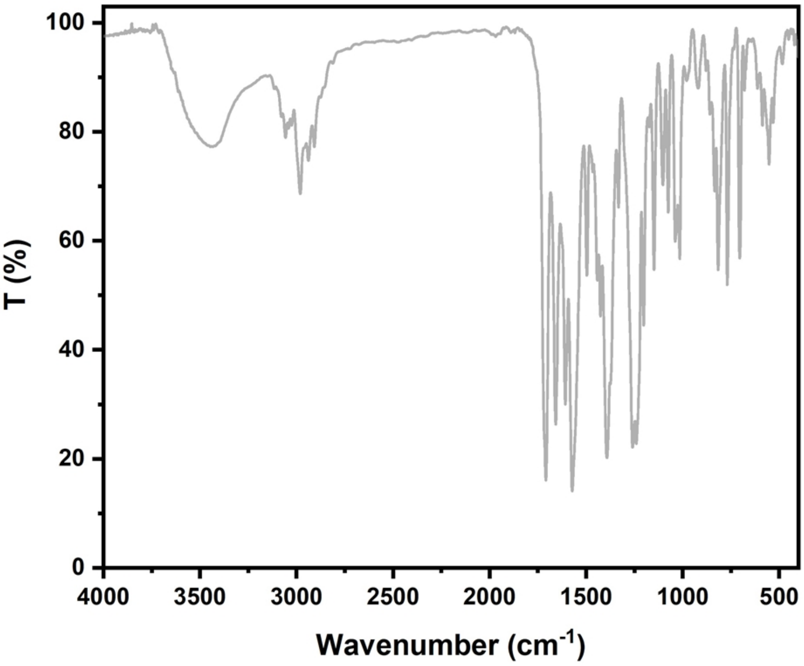


Figure S10. FT-IR spectra of **1**.

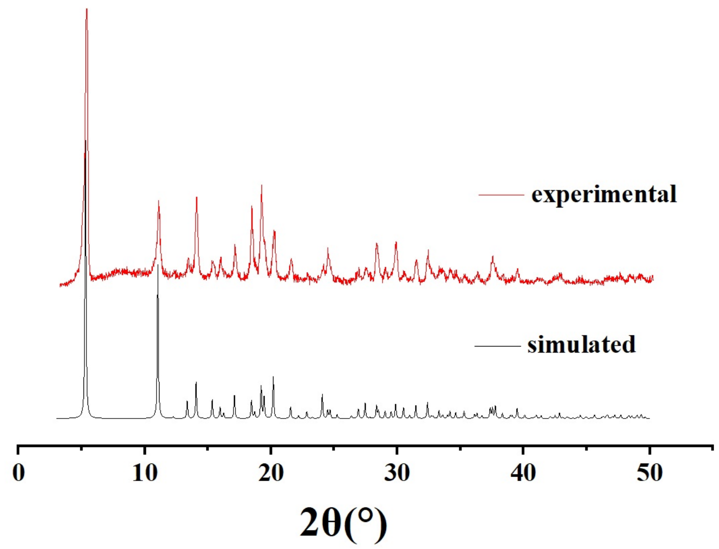


Figure S11. PXRD patterns of **2**.

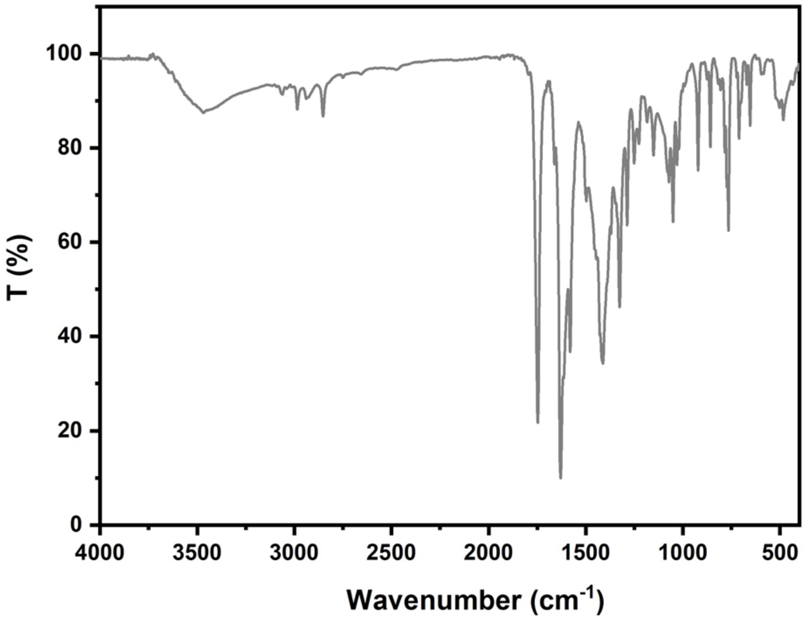


Figure S12. FT-IR spectra of **2**.

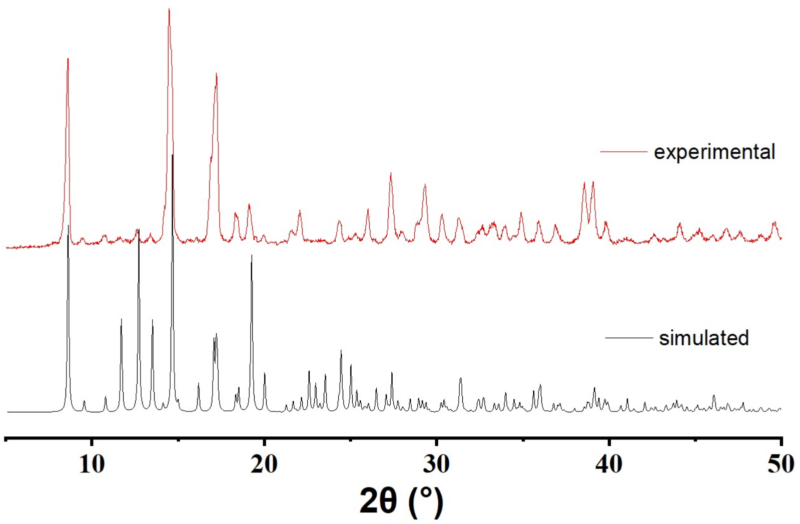


Figure S13. PXRD patterns of **3**.

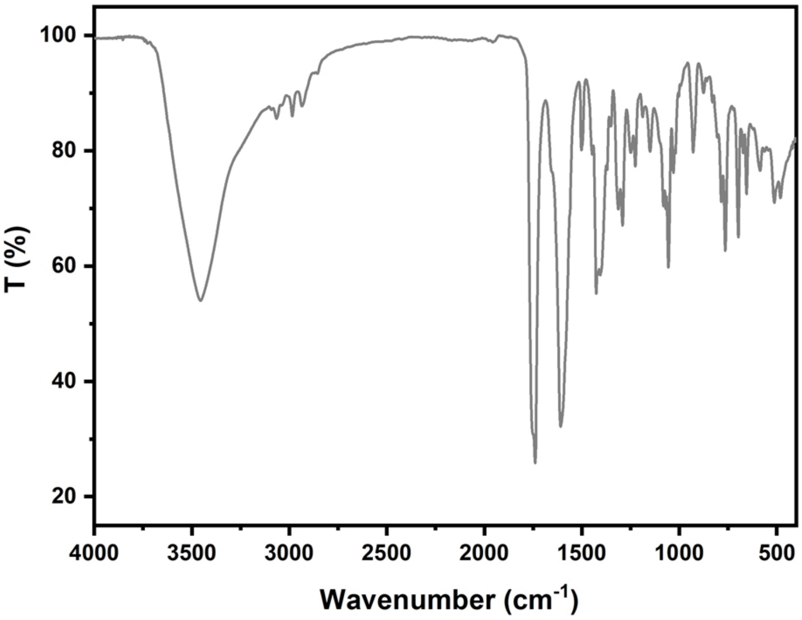


Figure S14. FT-IR spectra of **3**.

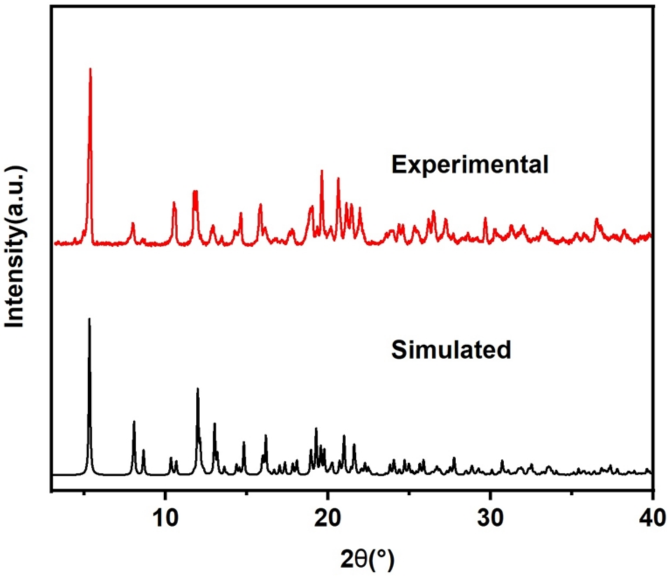


Figure S15. PXRD patterns of **4**.

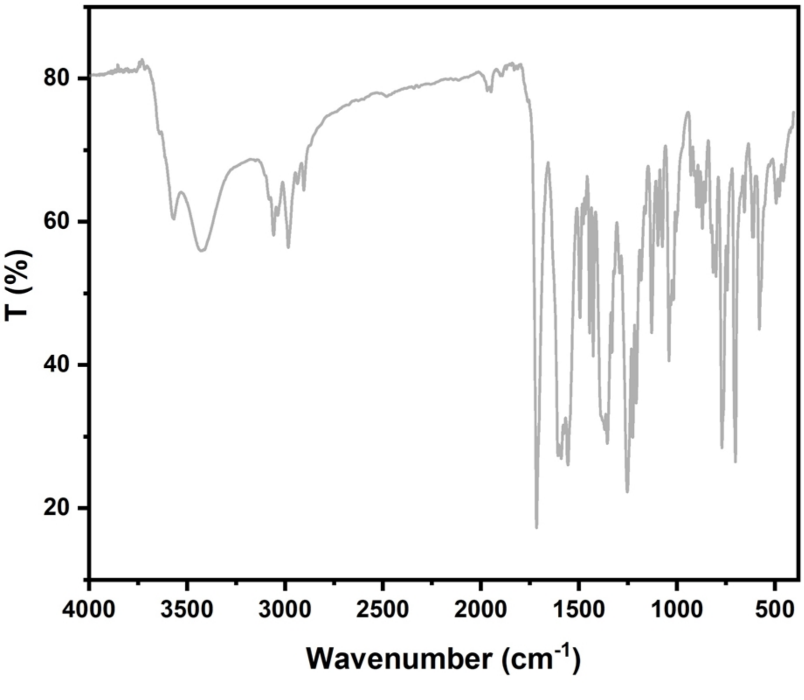
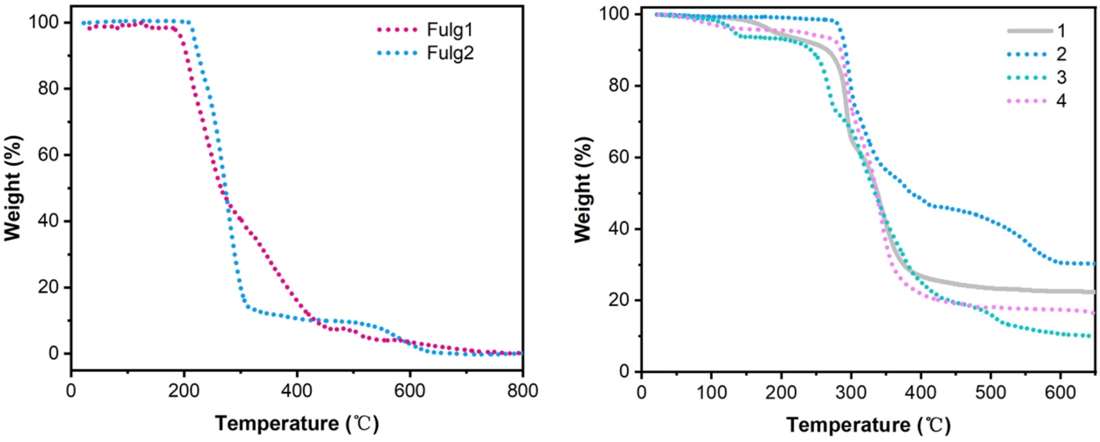
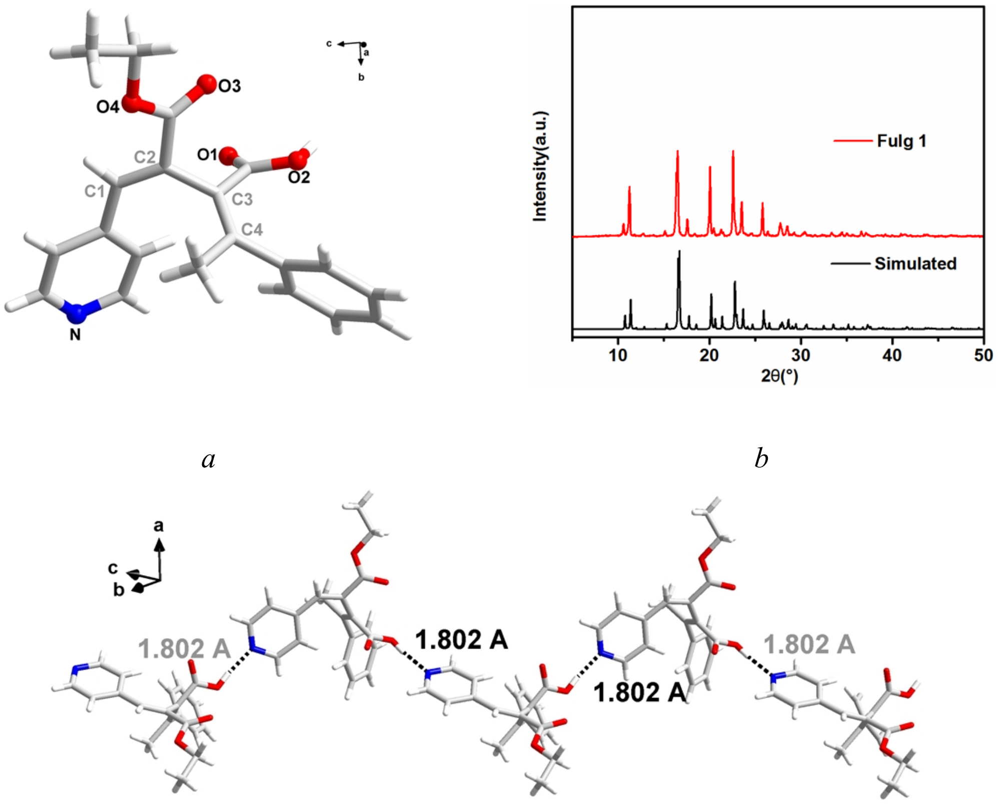


Figure S16. FT-IR spectra of **4**.



(*a*) (*b*)

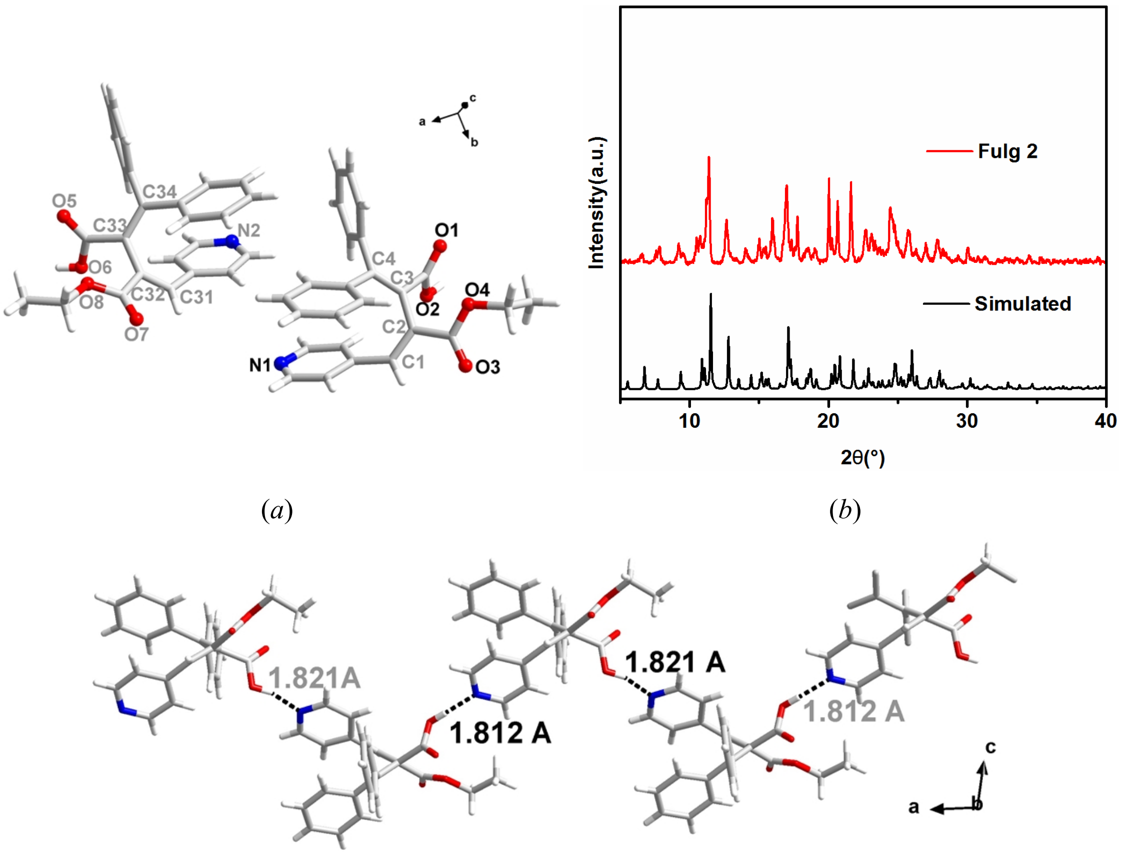
Figure S17. TGA traces for (*a*) both Fulg1 and Fulg2 and (*b*) their complexes **1-4**.



a *b*

c

Figure S18. (*a*) Molecular conformation of Fulg1 in *Z*-form; (*b*) PXRD pattern for Fulg1; (*c*) a 1 D infinite zigzag chain fabricated by the hydrogen bonding interactions between neighbouring Fulg1 molecules.



(*a*) (*b*)

(*c*)

Figure S19. (*a*) Molecular conformations of Fulg2 in *E*-form; (*b*) PXRD pattern for Fulg2; (*c*) a 1 D infinite zigzag chain fabricated by the hydrogen bonding interactions between neighbouring Fulg2 molecules.

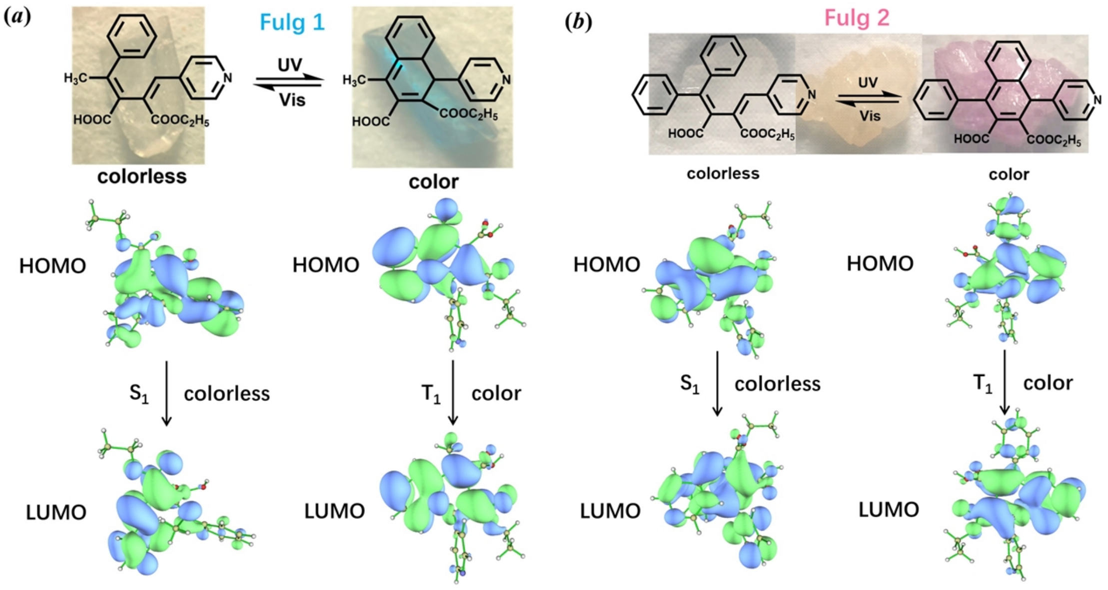
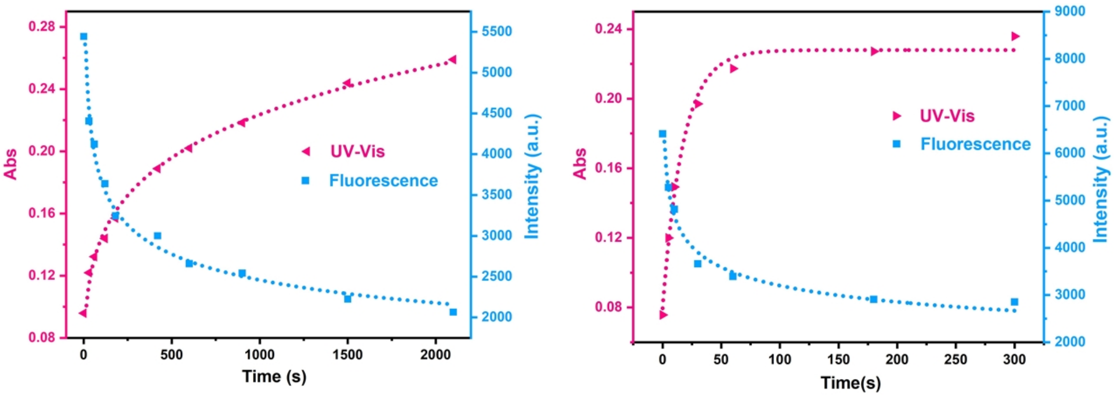


Figure S20. TD-DFT calculated frontier molecular orbitals for (a) Fulg1 and (b) Fulg2.



(*a*) (*b*)

Figure S21. Time dependence in peak intensities of UV-Vis diffuse-reflectance (red) and fluorescence (blue) for (*a*) **1** and (*b*) **4** under UV-lamp (313 nm) irradiation at different irradiation times.

Table S3. Calculated transition configurations for both Fulg1 and Fulg2 molecules.

molecule	color state	wavelength (nm)	transition configuration at S_1 state	transition proportion
Fulg 1	colorless	266.40	H-4→L	35.1%
			H-3→L	24.7%
			H-6→L	13.9%
			H→L+1	9.9%
			H-5→L	8.7%
Fulg 1	blue	445.83	H→L	99.5%
		276.24	H-4→L	55.5%
			H-1→L	17.3%
			H→L+3	8.1%
			H→L+4	7.4%
Fulg 2	colorless	284.55	H-1→L+1	85.6%
		254.61	H-5→L+1	68.1%
			H-6→L+1	6.9%
Fulg 2	purple	455.52	H→L	99.5%
		288.86	H-5→L	47.3%
			H-4→L	35.6%
			H→L+3	5.1%

References.

[S1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Jr. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 16*; Gaussian Inc., *Wallingford CT*, 2016.

[S2] T. Lu, F. W. Chen, Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem*. 2012, **33**, 580−592.

[S3] J. Zhang, T. Lu, Efficient evaluation of electrostatic potential with computerized optimized code. *Phys. Chem. Chem. Phys*. 2021, **23**, 20323–20328.