Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information for

Photoresponsive gadolinium–anthracene complexes: tuning the orientation and π–π stacking of anthracene groups via alkyl ester substituents of phosphonate ligands

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Table S1 Crystallographic data for compounds **1**, **2**, **2LT**, and **3**.

Compound	**1**	**2**	**2LT**	**3**
Formula	$C_{40}H_{46}GdN_5O_{16}P$	$C_{44}H_{54}GdN_5O_{16}P_2$	$C_{44}H_{54}GdN_5O_{16}P_2$	$C_{48}H_{62}GdN_5O_{16}P_2$
T / K	298(2)	300(2)	260(2)	300(2)
Mw	1072.01	1128.11	1183.59	1184.21
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P1$
a / Å	9.8914(6)	11.555(7)	10.9046(19)	10.0234(8)
b / Å	10.6271(7)	19.054(12)	11.0745(18)	11.1948(9)
c / Å	24.5080(14)	23.235(16)	23.236(4)	13.8853(11)
α / º	81.722(2)	90	87.693(5)	112.863(3)
β / º	80.060(2)	96.281(14)	88.109(5)	91.382(3)
γ / º	63.522(2)	90	61.649(5)	111.730(3)
V / Å^3	2264.8(2)	5085(6)	2467.1(7)	1307.71(18)
Z	2	4	2	1
ρ_{calcd} / g cm^{-3}	1.572	1.474	1.519	1.504
F(000)	1086	2300	1150	607
R_{int}	0.0372	0.0459	0.0298	0.0275
GooF	1.054	1.036	1.035	1.136
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0485, 0.1011	0.0543, 0.1312	0.0439, 0.1053	0.0354, 0.0628
R_1, wR_2 (all data)[a]	0.0650, 0.1075	0.0775, 0.1449	0.0578, 0.1132	0.0364, 0.0634
CCDC number	2191729	2191728	2191730	2191731

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (°) for **1** at 298 K.

Gd1-O1	2.322(3)	O4-Gd1-O12	126.91(13)
Gd1-O4	2.306(4)	O4-Gd1-O14	80.84(13)
Gd1-O5	2.468(4)	O5-Gd1-O7	51.16(14)
Gd1-O6	2.483(4)	O5-Gd1-O8	71.92(13)
Gd1-O8	2.531(4)	O5-Gd1-O10	86.46(13)
Gd1-O10	2.473(4)	O5-Gd1-O11	150.43(13)
Gd1-O11	2.541(5)	O5-Gd1-O12	140.77(14)
Gd1-O12	2.479(4)	O5-Gd1-O14	76.85(13)
Gd1-O14	2.346(3)	O7-Gd1-O8	102.29(15)
		O7-Gd1-O10	75.22(14)
O1-Gd1-O4	84.35(12)	O7-Gd1-O11	143.78(16)
O1-Gd1-O5	126.62(13)	O7-Gd1-O12	144.23(13)
O1-Gd1-O7	75.56(13)	O7-Gd1-O14	124.00(13)
O1-Gd1-O8	123.88(13)	O8-Gd1-O10	50.61(12)
O1-Gd1-O10	76.00(14)	O8-Gd1-O11	112.44(14)
O1-Gd1-O11	76.76(13)	O8-Gd1-O12	69.21(13)
O1-Gd1-O12	81.07(12)	O8-Gd1-O14	75.56(14)
O1-Gd1-O14	151.49(14)	O10-Gd1-O11	119.60(13)
O4-Gd1-O5	86.90(13)	O10-Gd1-O12	73.08(13)
O4-Gd1-O7	77.50(14)	O10-Gd1-O14	126.16(14)
O4-Gd1-O8	151.20(12)	O11-Gd1-O12	50.05(14)
O4-Gd1-O10	149.54(12)	O11-Gd1-O14	76.24(14)
O4-Gd1-O11	76.95(13)	O12-Gd1-O14	88.55(12)

Table S3 Selected bond lengths (Å) and angles (°) for **2** at 300 K.

Gd1-O1	2.307(5)	O4-Gd1-O8A	155.3(3)
Gd1-O4	2.287(6)	O4-Gd1-O8'A	49.7(3)
Gd1-O5/ O5'	2.529(9)/ 2.424(15)	O4-Gd1-O5'A	77.4(3)
Gd1-O6/ O6'	2.579(10)/ 2.456(13)	O4-Gd1-O6'A	124.7(3)
Gd1-O8/ O8'	2.512(12)/ 2.522(12)	O5-Gd1-O6	48.6(3)
Gd1-O8A/ O8'A	2.512(12)/ 2.522(12)	O1A-Gd1-O5	68.0(2)
Gd1-O5A	2.529(9)	O5-Gd1-O5A	169.3(3)
Gd1-O6A	2.579(10)	O5-Gd1-O6A	133.5(3)
Gd1-O1A	2.307(5)	O1A-Gd1-O6	116.3(2)
		O5A-Gd1-O6	133.5(3)
O1-Gd1-O4	79.33(14)	O6-Gd1-O6A	163.2(4)
O1-Gd1-O5	109.9(2)	O1A-Gd1-O8	82.9(3)
O1-Gd1-O6	67.1(2)	O8-Gd1-O8A	49.3(4)
O1-Gd1-O8	117.4(3)	O8-Gd1-O8'A	50.2(4)
O1-Gd1-O8'	130.9(3)	O1A-Gd1-O8'	70.4(3)
O1-Gd1-O5'	92.0(4)	O8A-Gd1-O8'	50.2(4)
O1-Gd1-O6'	84.1(3)	O8'-Gd1-O8'A	60.6(4)
O1-Gd1-O1A	158.7(2)	O5'-Gd1-O6'	50.8(4)
O1-Gd1-O5A	68.0(2)	O1A-Gd1-O5'	83.3(4)
O1-Gd1-O6A	116.3(2)	O5'-Gd1-O5'A	154.7(4)
O1-Gd1-O8A	82.9(3)	O5'-Gd1-O6'A	151.8(5)
O1-Gd1-O8'A	70.4(3)	O1A-Gd1-O6'	108.3(3)
O1-Gd1-O5'A	83.3(4)	O5'-Gd1-O6'	151.8(5)
O1-Gd1-O6'A	108.3(3)	O6'-Gd1-O6'A	110.7(4)
O4-Gd1-O5	84.6(2)	O1A-Gd1-O5A	109.9(2)
O4-Gd1-O6	98.4(3)	O1A-Gd1-O6A	67.1(2)
O4-Gd1-O8	155.3(3)	O1A-Gd1-O8A	117.4(3)
O4-Gd1-O8'	149.7(3)	O1A-Gd1-O8'A	130.9(3)
O4-Gd1-O5'	77.4(3)	O1A-Gd1-O5'A	92.0(4)
O4-Gd1-O6'	124.7(3)	O1A-Gd1-O6'A	84.1(3)
O1A-Gd1-O4	79.33(14)	O5A-Gd1-O6A	48.6(3)
O4-Gd1-O5A	84.6(2)	O5'A-Gd1-O6'A	50.8(4)
O4-Gd1-O6A	98.4(3)		

Table S4 Selected bond lengths (Å) and angles (°) for **3** at 300 K.

Gd1-O1	2.330(5)	O4-Gd1-O12	130.4(2)
Gd1-O4	2.320(6)	O4-Gd1-O14	82.86(19)
Gd1-O5	2.486(7)	O5-Gd1-O7	50.78(19)
Gd1-O6	2.528(6)	O5-Gd1-O8	72.5(2)
Gd1-O8	2.525(7)	O5-Gd1-O10	80.9(2)
Gd1-O10	2.464(7)	O5-Gd1-O11	151.8(2)
Gd1-O11	2.522(7)	O5-Gd1-O12	141.4(2)
Gd1-O12	2.495(7)	O5-Gd1-O14	78.98(18)
Gd1-O14	2.341(4)	O7-Gd1-O8	105.1(2)
O1-Gd1-O4	86.13(19)	O7-Gd1-O10	73.5(2)
O1-Gd1-O5	124.11(17)	O7-Gd1-O11	144.4(2)
O1-Gd1-O7	73.58(19)	O7-Gd1-O12	140.4(2)
O1-Gd1-O8	125.2(2)	O7-Gd1-O14	126.1(2)
O1-Gd1-O10	78.6(2)	O8-Gd1-O10	50.68(19)
O1-Gd1-O11	79.05(19)	O8-Gd1-O11	109.1(2)
O1-Gd1-O12	78.8(2)	O8-Gd1-O12	69.0(2)
O1-Gd1-O14	153.47(19)	O8-Gd1-O14	70.9(2)
O4-Gd1-O5	85.2(2)	O10-Gd1-O11	122.8(2)
O4-Gd1-O7	75.7(2)	O10-Gd1-O12	73.6(2)
O4-Gd1-O8	148.1(2)	O10-Gd1-O14	121.5(2)
O4-Gd1-O10	14 8.42(18)	O11-Gd1-O12	50.7(2)
O4-Gd1-O11	80.3(2)	O11-Gd1-O14	75.3(2)
O1-Gd1-O4	86.13(19)	O12-Gd1-O14	90.2(2)

Table S5 Intramolecular and intermolecular hydrogen bonding interactions.

Compound **1**			
D-H···A	$d_{H\cdots A}$ / Å	$d_{D\cdots A}$ / Å	$Angle_{D-H\cdots A}$ / °
C17-H17C···O9	2.637	3.544	157.8
C13-H13···O10	2.680	3.581	163.2
C35-H35B···O9	2.598	3.439	146.6
C7-H7···π (C36, dmpu)	2.835	3.710	157.8
Compound **2**			
C17-H17B···O7	2.687	3.714	158.8
C17-H17B···O7’	2.813	3.596	157.0
C7-H7···O7	2.577	3.394	146.7
C7-H7···O7’	2.748	3.620	156.5
C11-H11···O9	2.531	3.356	147.8
C12-H12···O7	2.640	3.321	130.66
C12-H12···O7’	2.939	3.662	135.6
C20-H20B···O9	2.568	3.457	154.3
C19-H19B···N1	3.382	4.143	137.68
Compound **3**			
C9-H9···O13	2.667	3.564	162.5
C13-H13···O10	2.672	3.560	160.1
C26-H26···π(C40)	2.784	3.609	148.3
C36-H36A···N4	2.808	3.591	139.3
C36-H36C···N5	3.30	3.679	103.8

Table S6 Selected bond lengths (Å) and bond angles (°) for **2LT** at 260 K.

Gd1-O1	2.329(3)	O4-Gd1-O14	84.22(15)
Gd1-O4	2.287(5)	O5-Gd1-O6	51.13(13)
Gd1-O5	2.485(4)	O5-Gd1-O8	71.59(14)
Gd1-O6	2.465(5)	O5-Gd1-O10	104.56(14)
Gd1-O8	2.473(5)	O5-Gd1-O11	145.80(15)
Gd1-O10	2.538(5)	O5-Gd1-O12	135.12(14)
Gd1-O11	2.504(5)	O5-Gd1-O14	73.79(13)
Gd1-O12	2.485(4)	O6-Gd1-O8	79.90(16)
Gd1-O14	2.323(4)	O6-Gd1-O10	72.86(16)
O1-Gd1-O4	79.88(14)	O6-Gd1-O11	155.42(13)
O1-Gd1-O5	128.08(12)	O6-Gd1-O12	139.57(17)
O1-Gd1-O6	80.78(13)	O6-Gd1-O14	124.87(13)
O1-Gd1-O8	123.48(14)	O8-Gd1-O10	50.39(12)
O1-Gd1-O10	73.20(14)	O8-Gd1-O11	119.17(15)
O1-Gd1-O11	75.66(13)	O8-Gd1-O12	70.43(15)
O1-Gd1-O12	93.04(13)	O8-Gd1-O14	81.01(15)
O1-Gd1-O14	149.46(15)	O10-Gd1-O11	106.27(15)
O4-Gd1-O5	80.49(14)	O10-Gd1-O12	67.15(16)
O4-Gd1-O6	88.52(16)	O10-Gd1-O14	126.51(15)
O4-Gd1-O8	151.09(12)	O11-Gd1-O12	49.96(16)
O4-Gd1-O10	149.22(14)	O11-Gd1-O14	76.14(13)
O4-Gd1-O11	80.63(15)	O12-Gd1-O14	77.50(14)
O4-Gd1-O12	129.96(15)		

Table S7. Metal-anthracene complexes capable of photocycloaddition reaction in the solid state.

Compound	$d_{C\text{-}C}$	SC-SC	reversible	Ref.
$(nBu_4N)_4[Cu_2(anba)_2]$	3.698	×	√ (bulk)	S1
$[Ag(MAMA)_2]PF_6$	3.698	×	n.a.	S2
$[Ag(MAMA)_2]BF_4$	3.685	×	n.a.	S2
$[Ag(MAMA)_2][Ag(NO_3)_2]$	3.819	×	n.a.	S2
$[Pt(BA2DA)_2Cl_2]$	3.503	√	√ (bulk)	S3
Au(2-naphthyl)(L^1)	3.891	√	n.a.	S4
$[Eu_2(hfa)_6(Ant)_2]$	3.958	√	n.a.	S5
$[Dy(NO_3)_3(L^{Et})_3]$	3.739	×	√ (on surface)	S6
$[Dy(NO_3)_3(L^{Et})(hmpa)_2]$	3.771	√	√ (bulk)	S7
$[Gd(NO_3)_3(L^{Et})(hmpa)_2]$	3.765	√	√ (bulk)	S7
$[Dy(NO_3)_3(L^{Et})(temdp)]$	3.769	×	×	S8
$[Dy(NO_3)_3(L^{Me})(temdp)]$	3.745	×	×	S8
$[Dy(SCN)_3(L^{Et})_2(4\text{-hpy})_2]$	3.786	×	√ (bulk)	S9
$[DyX_3(L^{Et})_3]$ (X = Cl, Br)	3.78-3.94	×	√ (on surface)	S10
$[Dy_2(SCN)_4(L^2)_2(L^{Me})_4]$	3.687	√	√ (bulk)	S11
$[Gd(NO_3)_3(L^{Me})_2(dmpu)]$	3.681	×	√ (bulk)	This work
$[Gd(NO_3)_3(L^{Et})_2(dmpu)]$	3.963	×	√ (bulk)	This work

Abbreviation: nBu_4N^+ = tetra-n-butylammonium cation, H_4anba = N,N'-2,6-anthracenebis(oxamic acid), BA2DA = 1,2-Bis[(anthracen-9-ylmethylene) amino] ethane, MAMA = 9-(methylaminomethyl)anthracene, L^1 = isocyanoanthracene, Ant = 1,5-bis(diphenylphosphoryl)anthracene, hfac = hexafluoroacetylacetonate, temdp = tetraethylmethylenediphosphonate, 4-hpy = hydroxypyridine, HL^2 = 4-methyl-2,6-dimethoxyphenol. SC-SC = single crystal-to-single crystal transformation, n.a. = not available

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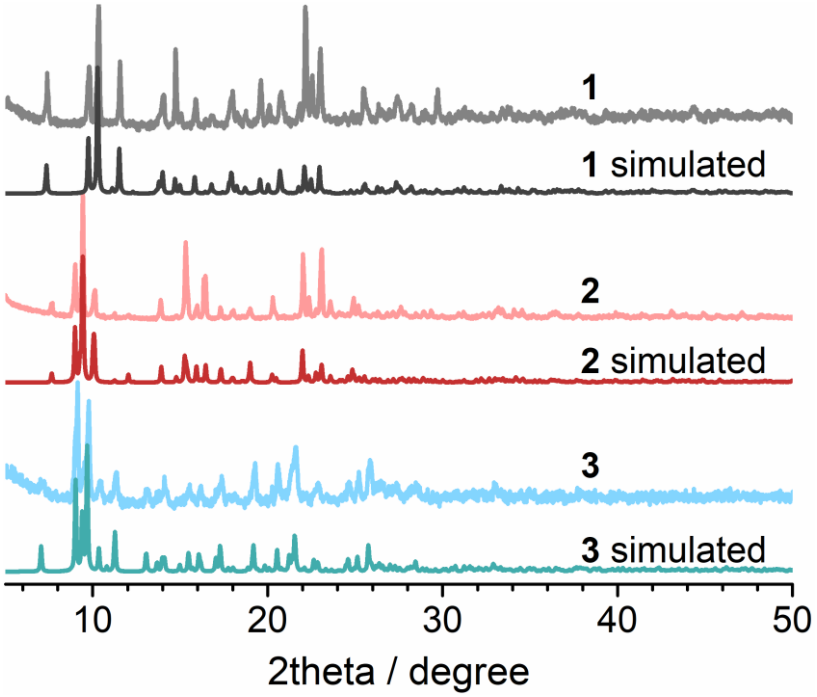

Fig. S1 The PXRD patterns for powder samples of **1**, **2** and **3** compared with their simulated patterns from corresponding crystal structures.

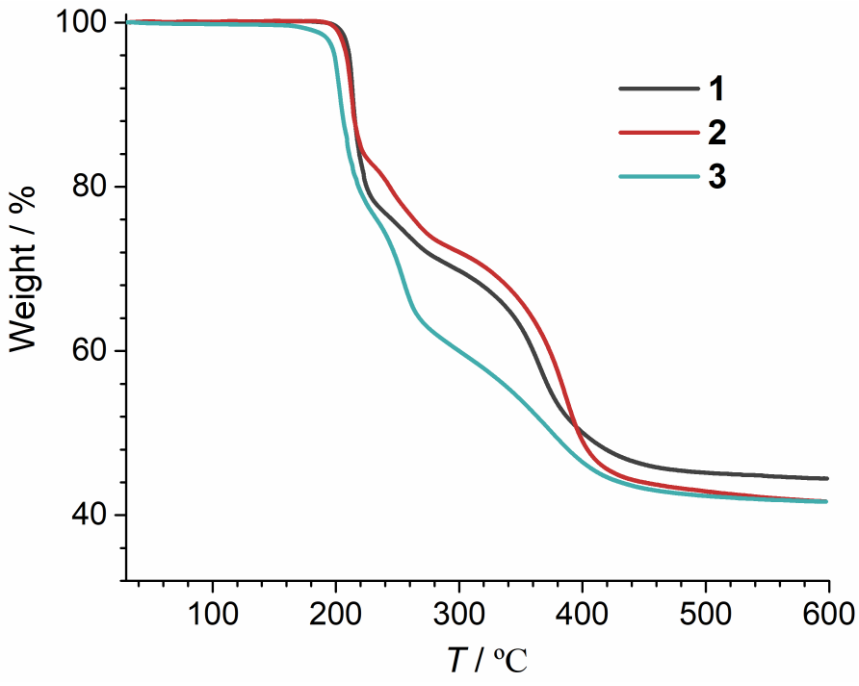

Fig. S2 The thermogravimetric curves for compounds **1**, **2** and **3** between 30 - 600 ^{o}C.

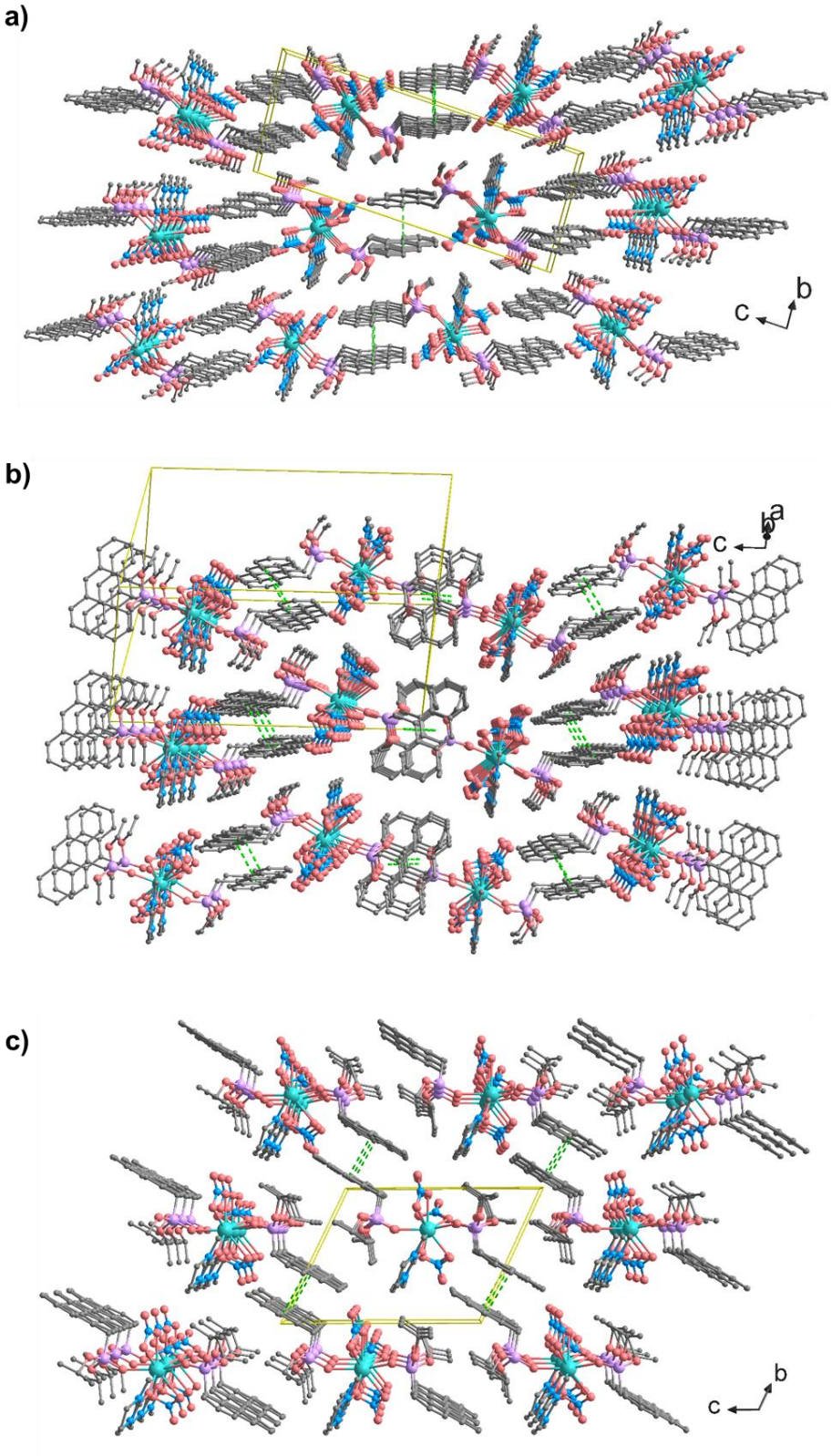

Fig. S3 Packing diagrams of structures for compounds **1** (a), **2** (b) and **3** (c).

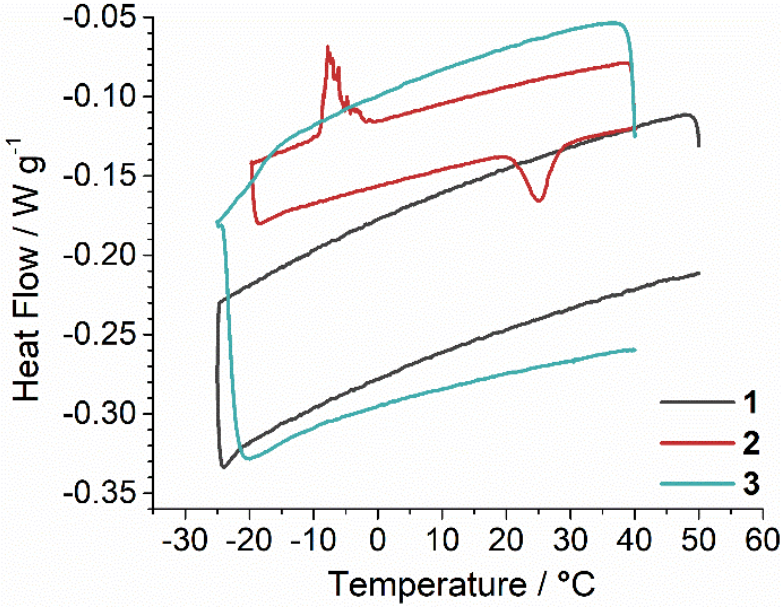

Fig. S4 The DSC curves of compounds **1-3**.

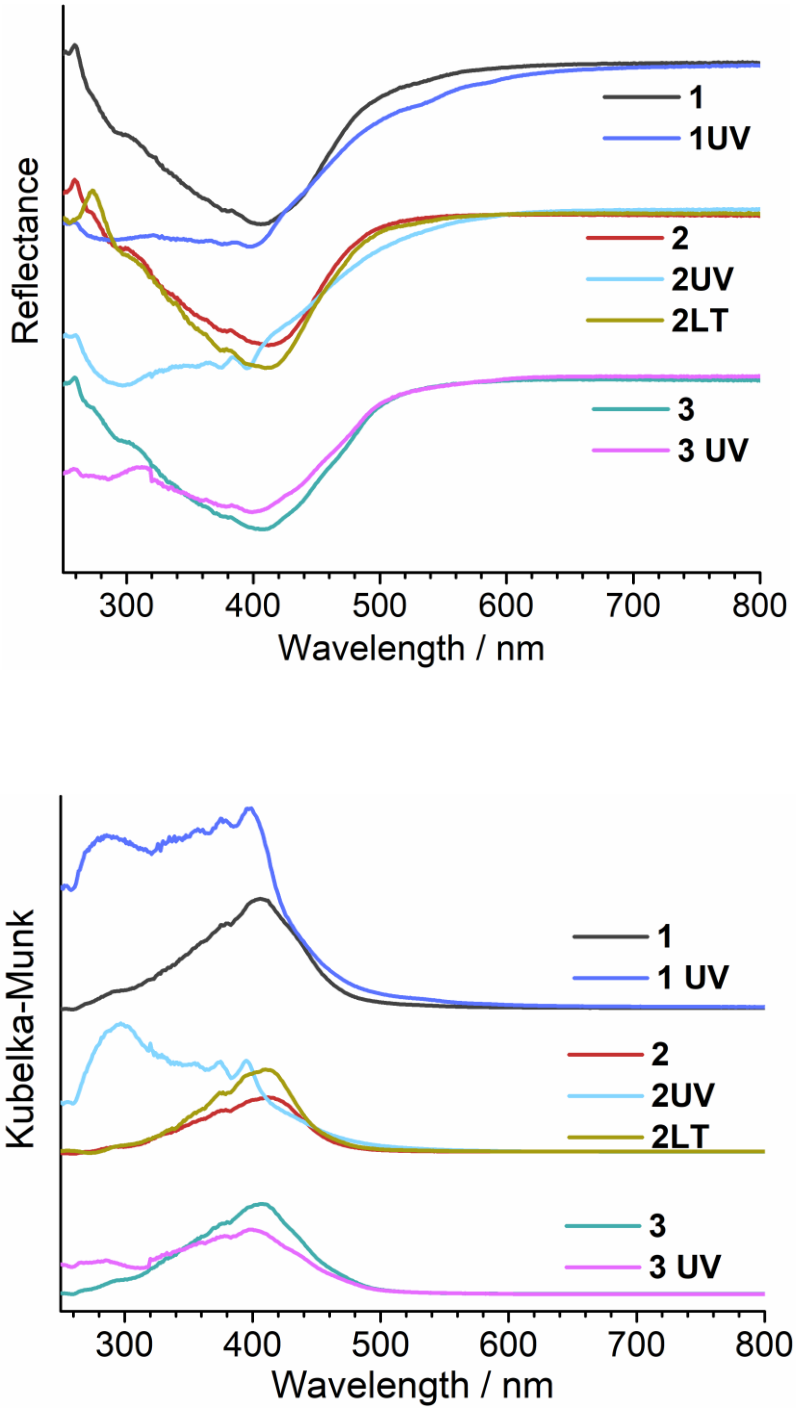

Fig. S5 The UV-vis diffused reflectance spectra (top) and corresponding Kubelka-Munk functions: $F(R)=(1-R)^2/2R$ (bottom) for all compounds before and after irradiation with LED UV light.

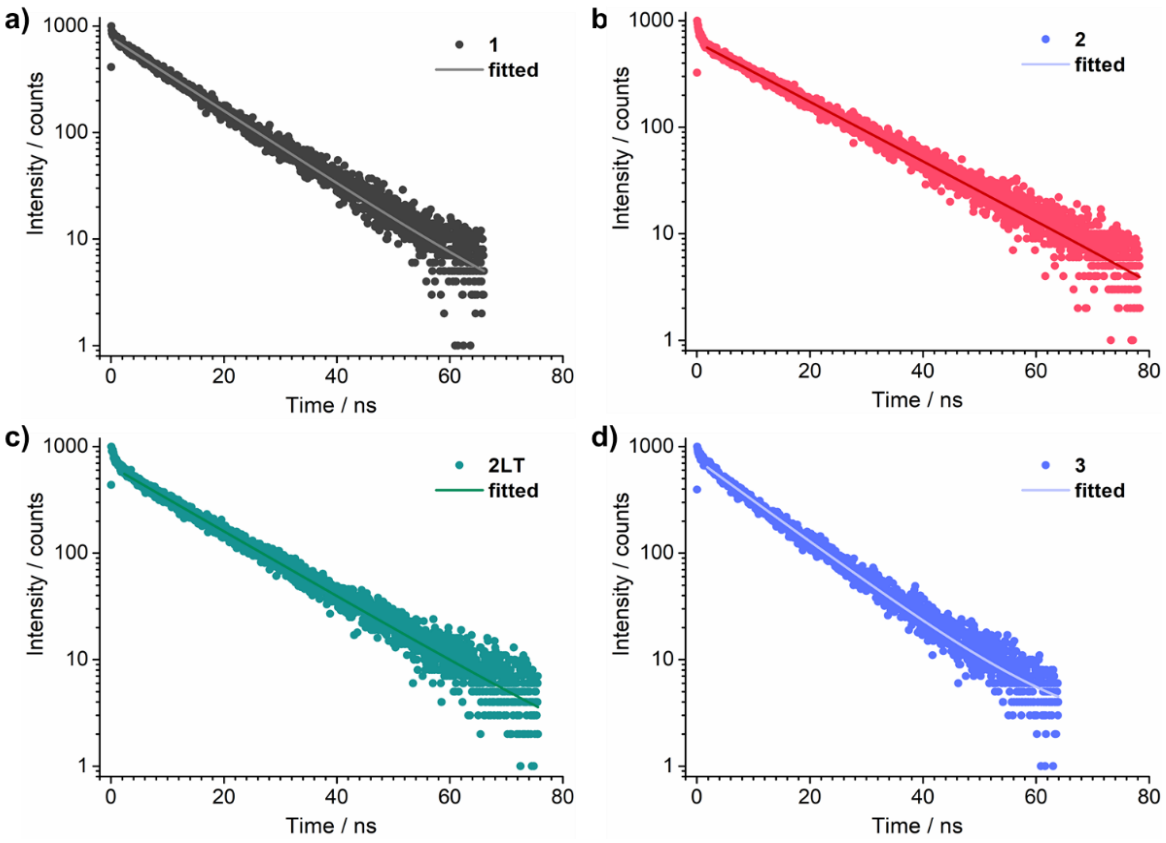

Fig. S6 The fluorescent decay curves for compounds **1**, **2**, **2LT** and **3** excited at 374 nm. The decay profiles were fitted reasonably well to a single exponential function for obtaining the lifetime value via the software DAS6.

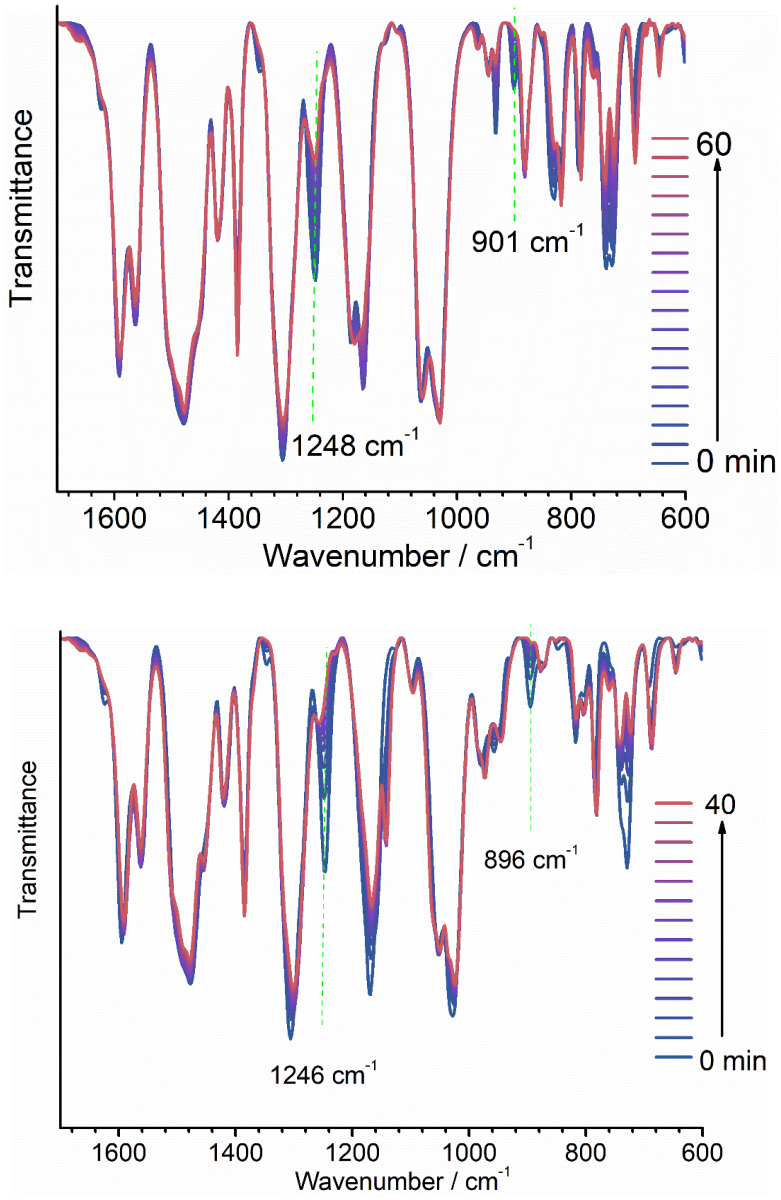

Fig. S7 Time-dependent in-situ IR spectra for **1** (top) and **2** (bottom) exposed to 395 nm UV light for different period of time.

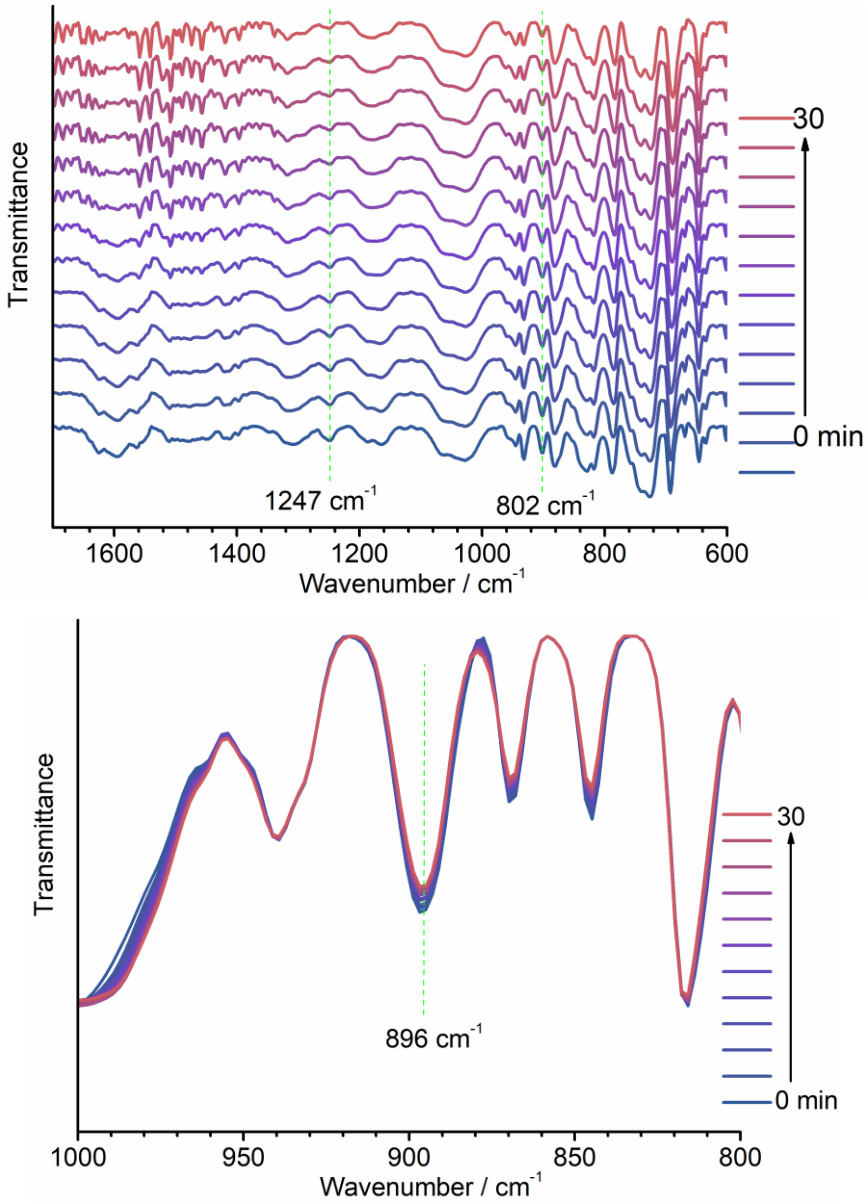

Fig. S8 Time-dependent in-situ IR spectra for **3** exposed to 395 nm UV light up to 30 min shown in wavenumber range of 1700-600 cm^{-1} (top) and 1000-800 cm^{-1} (bottom).

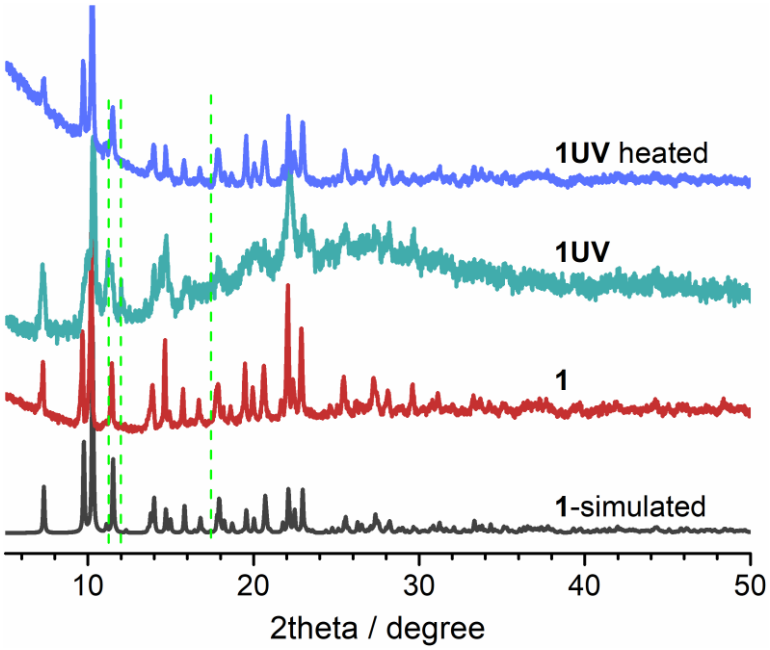

Fig. S9 The PXRD patterns for **1**, **1UV** given by irradiation of **1** with 395 nm UV light for 5 hours, and the heated sample of **1UV** at 130 °C.

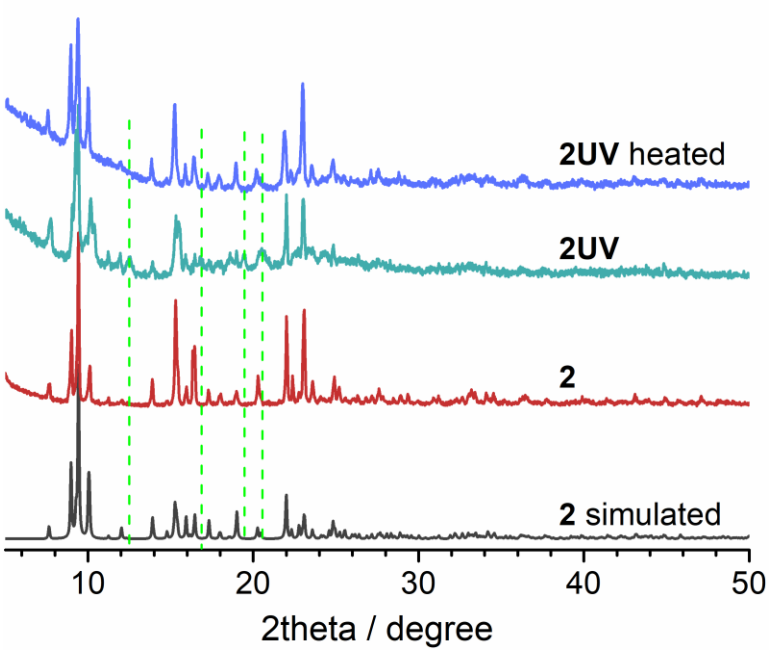

Fig. S10 The PXRD patterns for **2**, **2UV** given by irradiation of **2** with 395 nm UV light for 3 hours, and the heated sample of **2UV** at 150 °C.

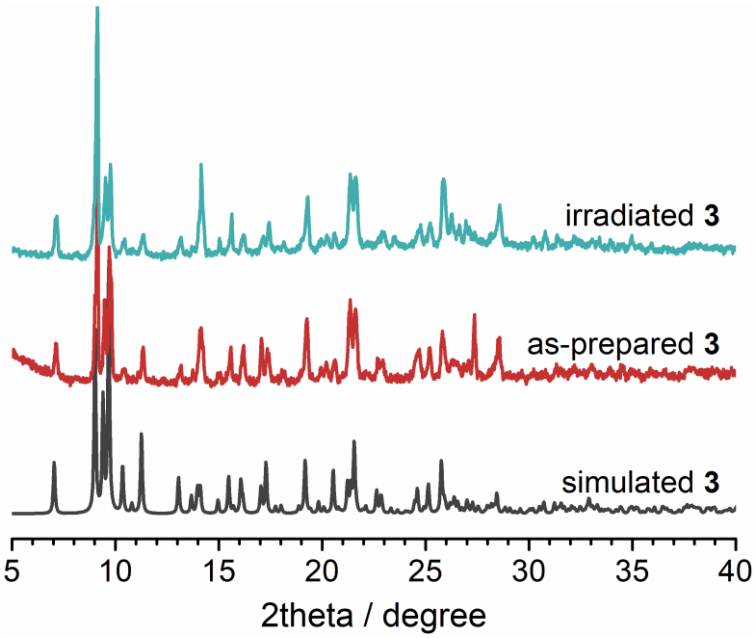

Fig. S11 The PXRD patterns for **3** exposed to 395 nm UV for 5 hours.

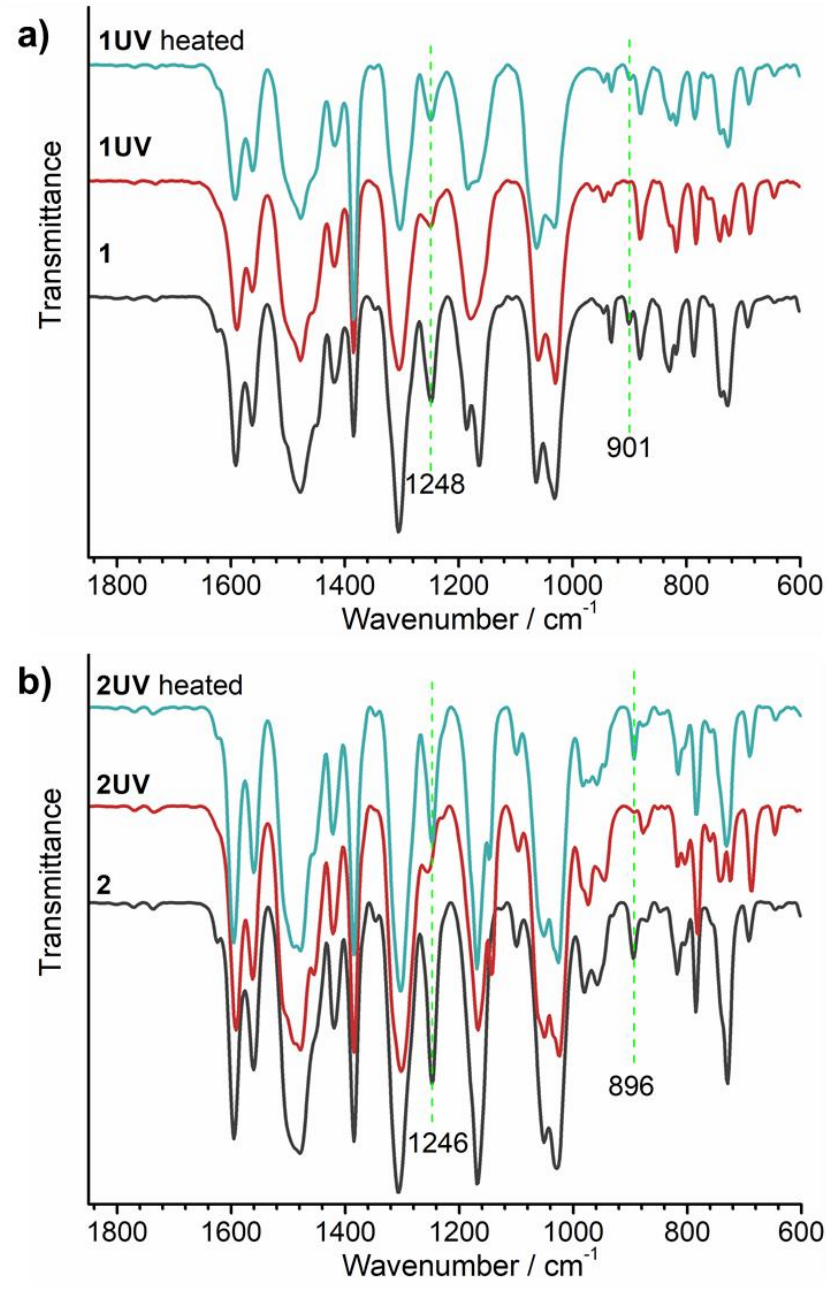

Fig. S12 The reversed IR spectra for compound **1** and **2** after exposed to UV light and final thermal annealing 150 °C.

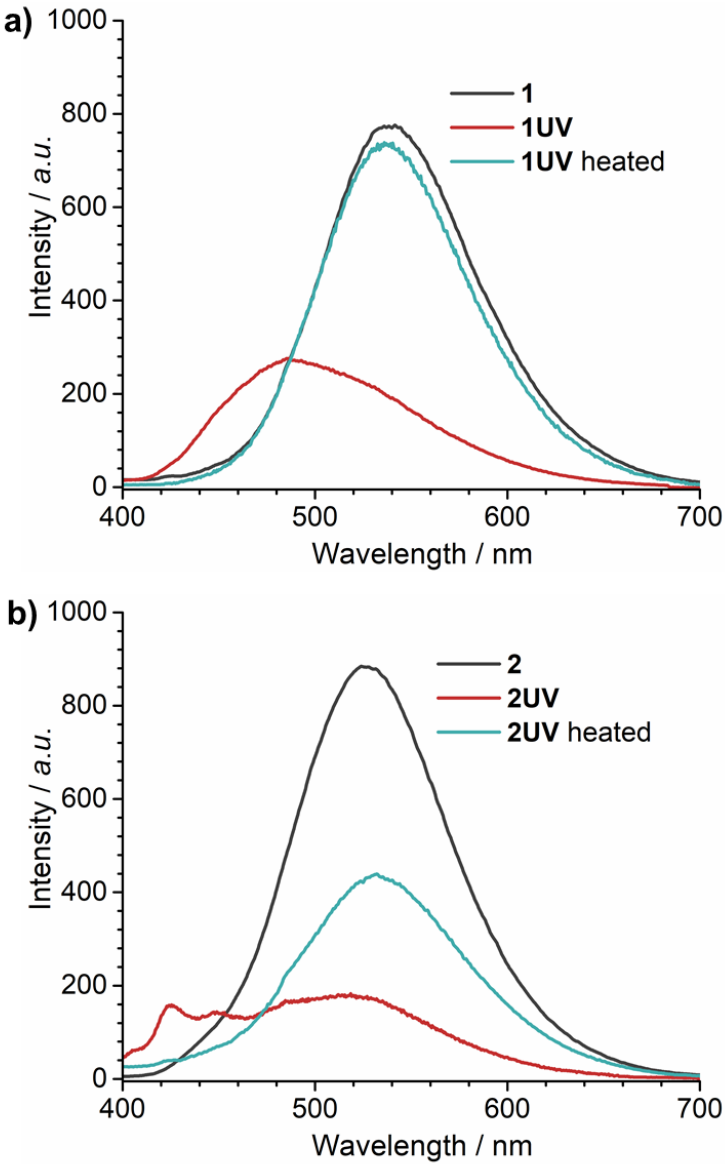

Fig. S13 The reversed emission spectra for compound **1** and **2** after exposed to UV light and final thermal annealing at 130 and 150 °C.

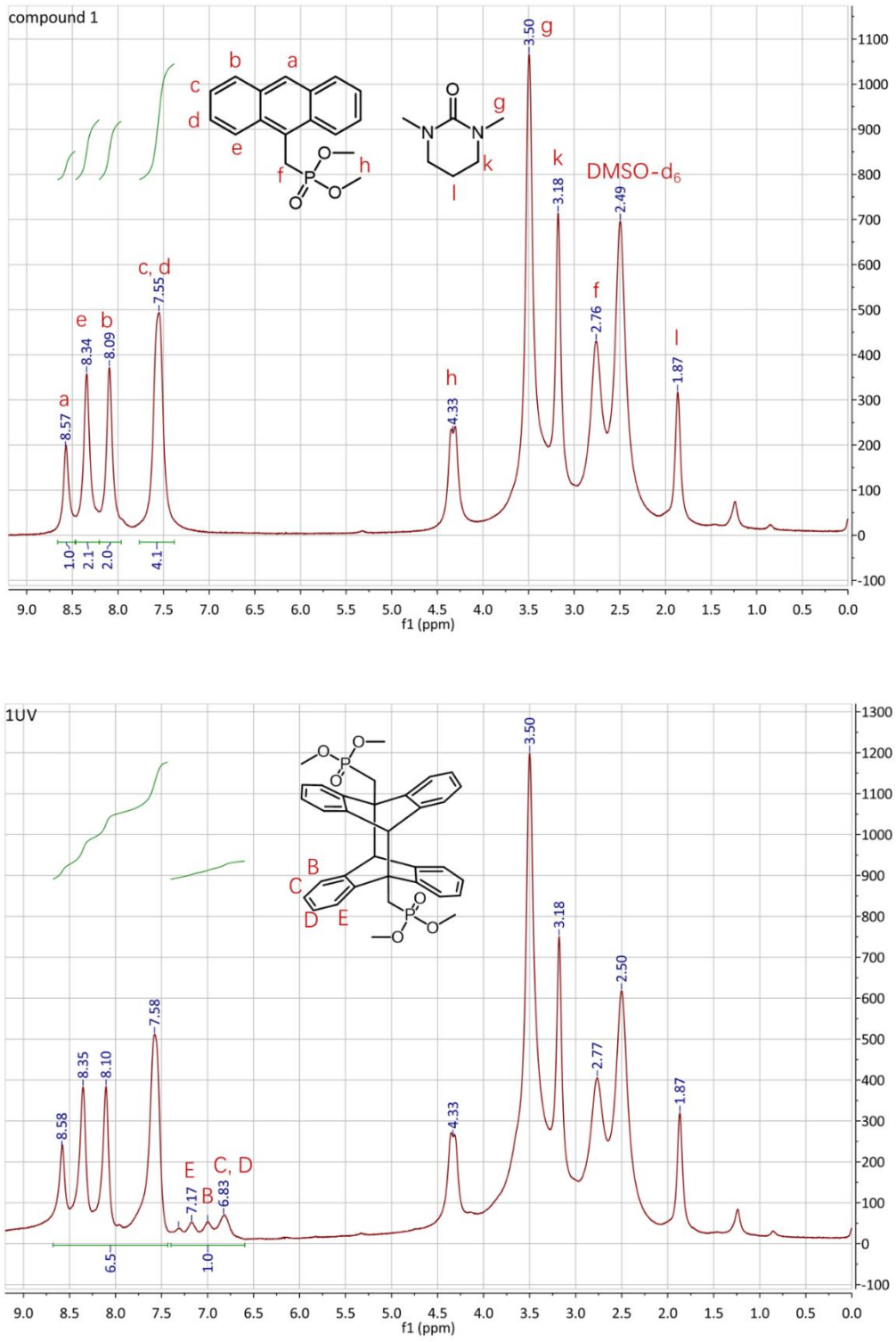

Fig. S14 The ^{1}H NMR spectrum of compounds **1** and **1UV** in DMSO-d_6. The irradiation of **1** upon 395 nm UV light for 3 hours gave the sample **1UV**.

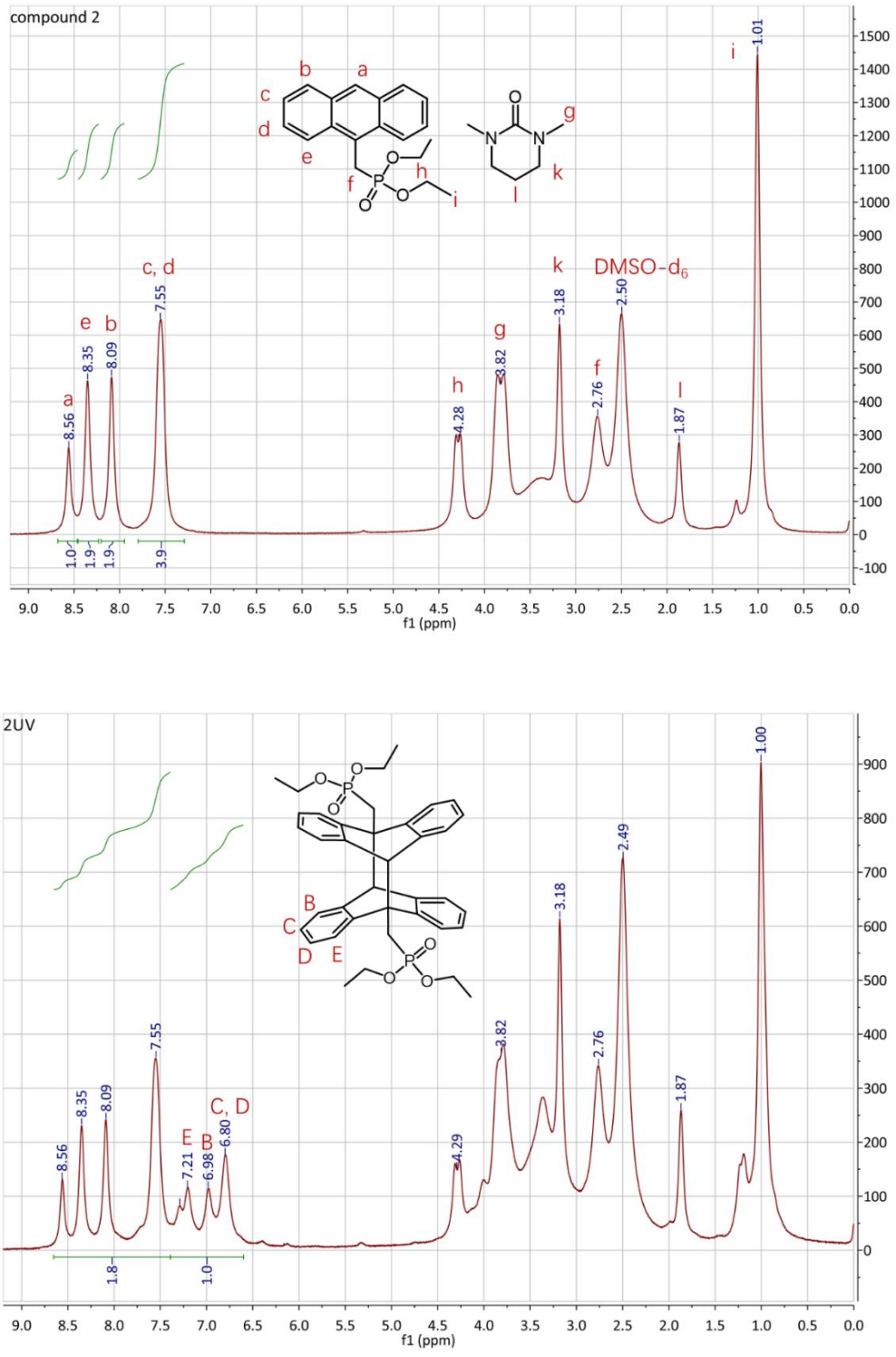

Fig. S15 The ^{1}H NMR spectrum of compounds **2** and **2UV** in DMSO-d_6. The irradiation of **2** upon 395 nm UV light for 3 hours gave the sample **2UV**.