Supporting Information For

Studies of The Isomerization and Photophysical Properties of a Novel Ligand based on 2,2′:6′,2″-Terpyridine and its Complexes

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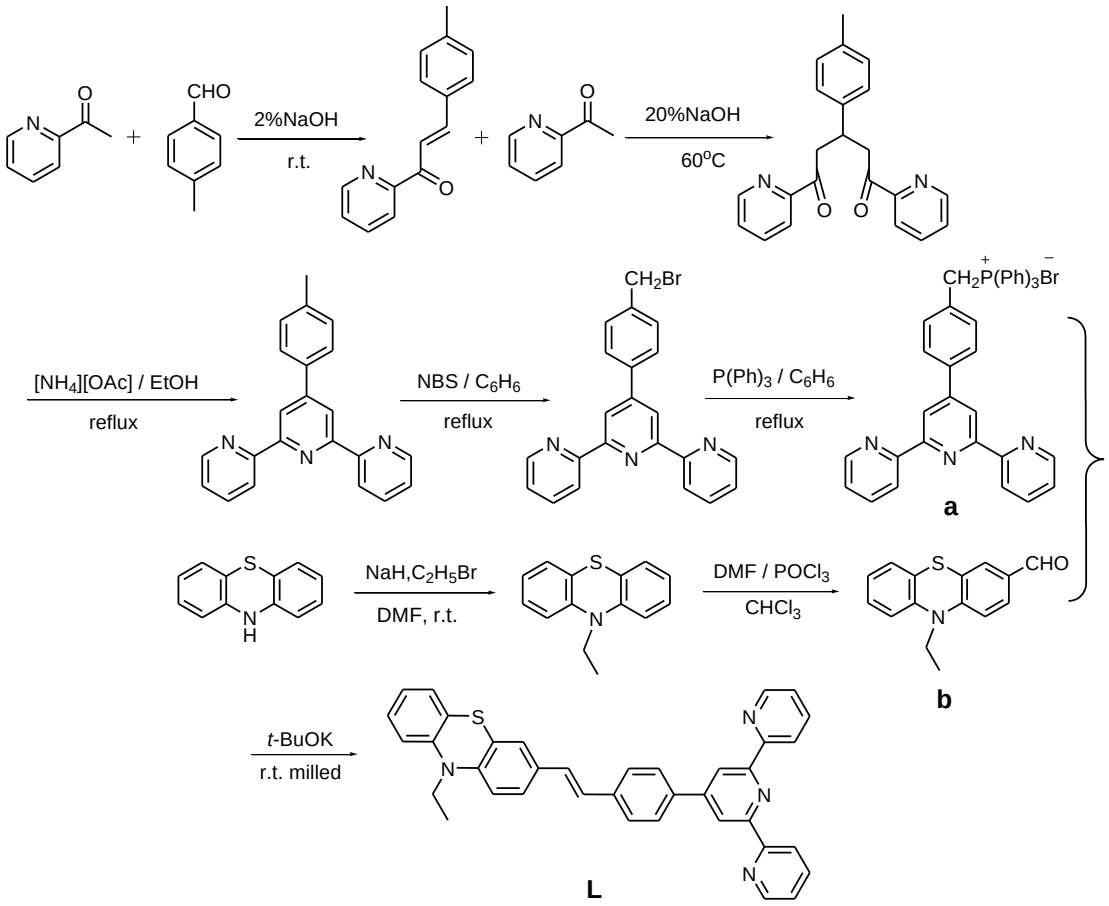
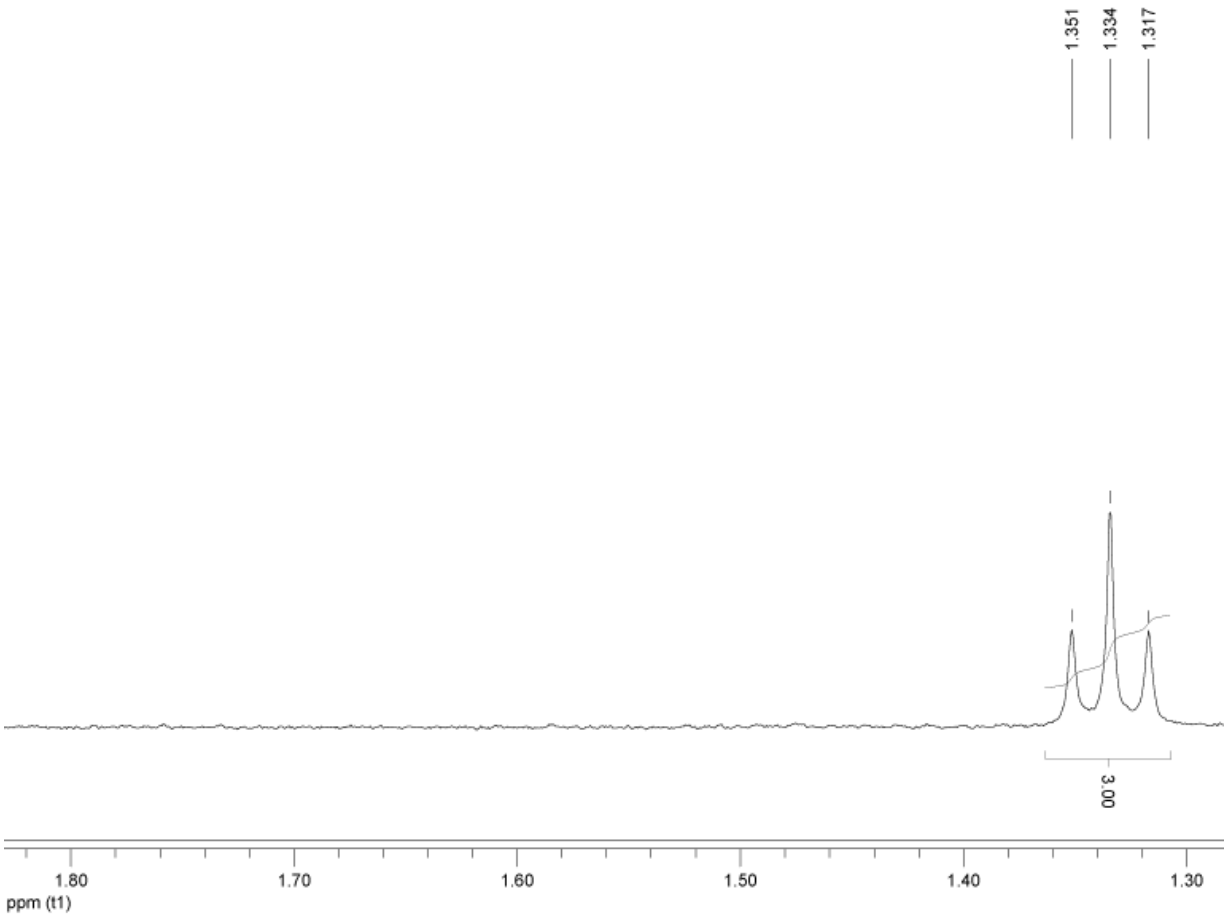
Experimental section



Scheme S1. Synthetic routes of **L**.

Materials and Apparatus. All solvents were dried and purified by usual methods. Elemental analysis was performed with a Perkin–Elmer 240 analyzer. IR spectra (4000–400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT–IR 170 SX spectrophotometer. The mass spectra were obtained on a Micromass GCT–MS Spectrometer. ^{1}H and ^{13}C NMR spectra were performed on Bruker 400 spectrometer with TMS as the internal standard. Thermogravimetric analysis (TGA) analysis was recorded with a Perkin–Elmer Pris–1 DMDA–V1 analyzer in an atmosphere of nitrogen at a heating rate of 10 °C·min^{-1}.

Optical measurements. The OPA spectra were measured on a UV−3600 Spectrophotometer. The OPEF measurements were performed using a F−2500 Fluorescence Spectrophotometer. The OPA and OPEF of **L** were measured in six solvents with the concentration of 1.0×10^{-5} M, while those of the complexes were measured in DMF dilute solutions (1.0×10^{-5} M). The third-order nonlinear optical (NLO) properties of all the compounds were studied by the *Z*-scan technique under an open aperture configuration with 532 nm laser pulses of 18 ns using DMF dilute solutions (1.5×10^{-4} M).



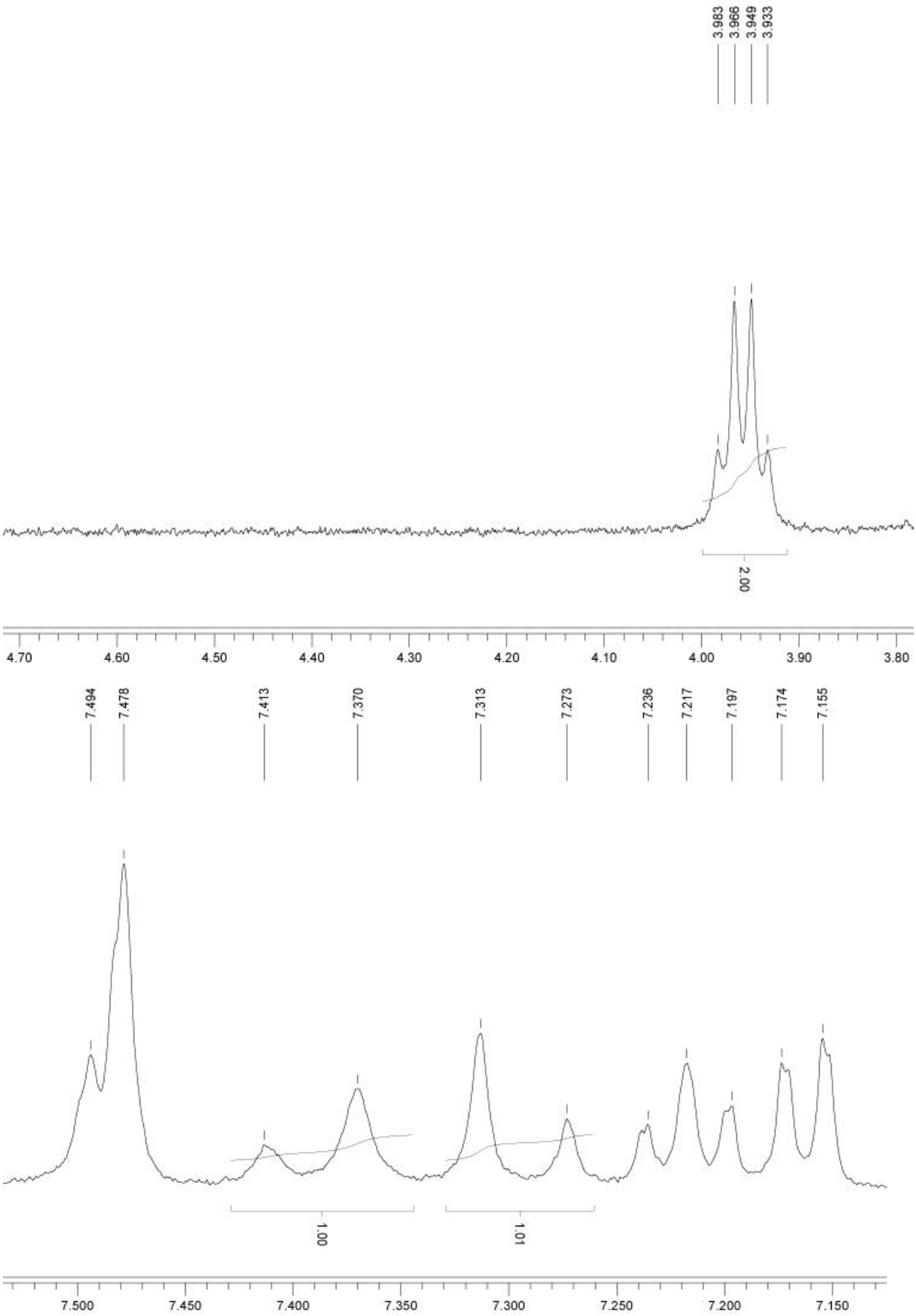
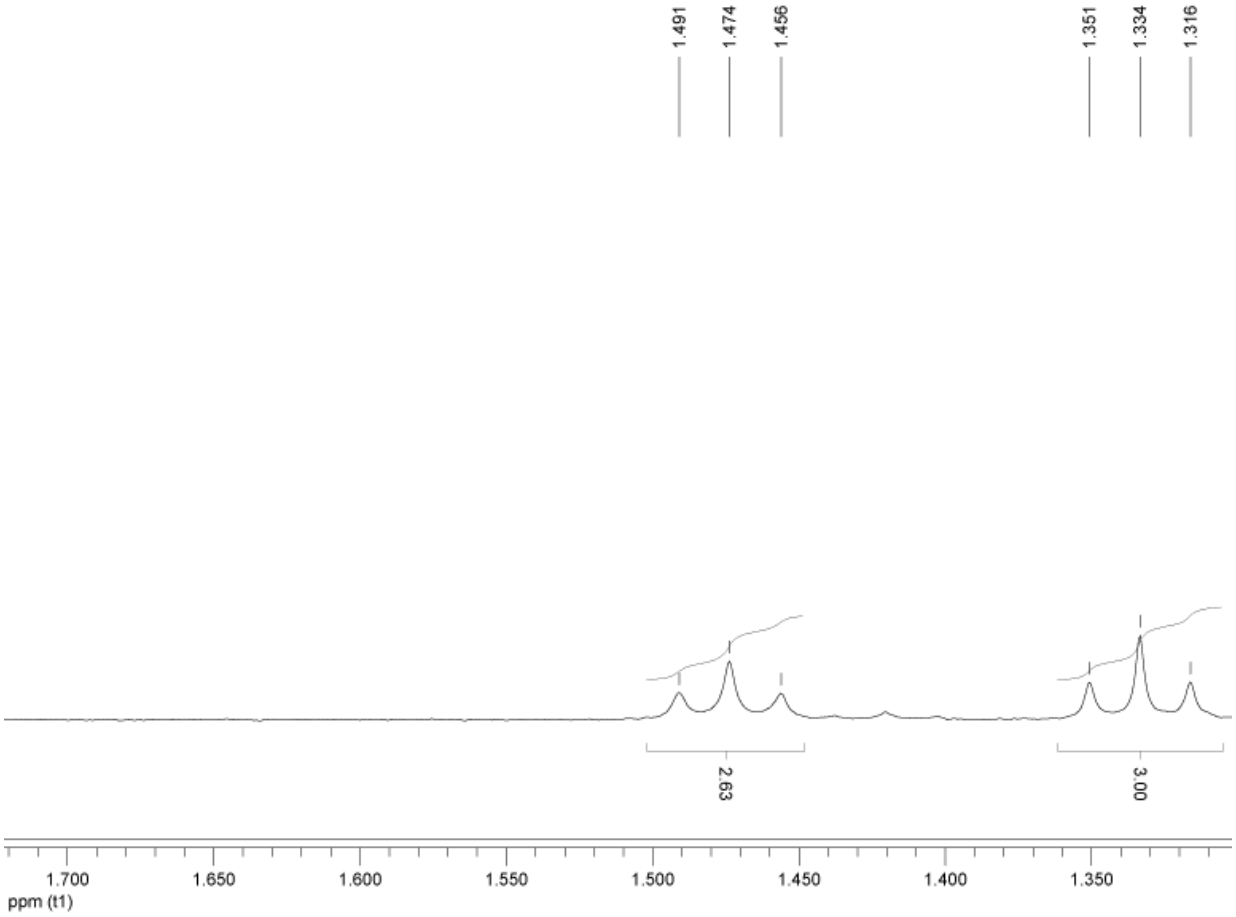
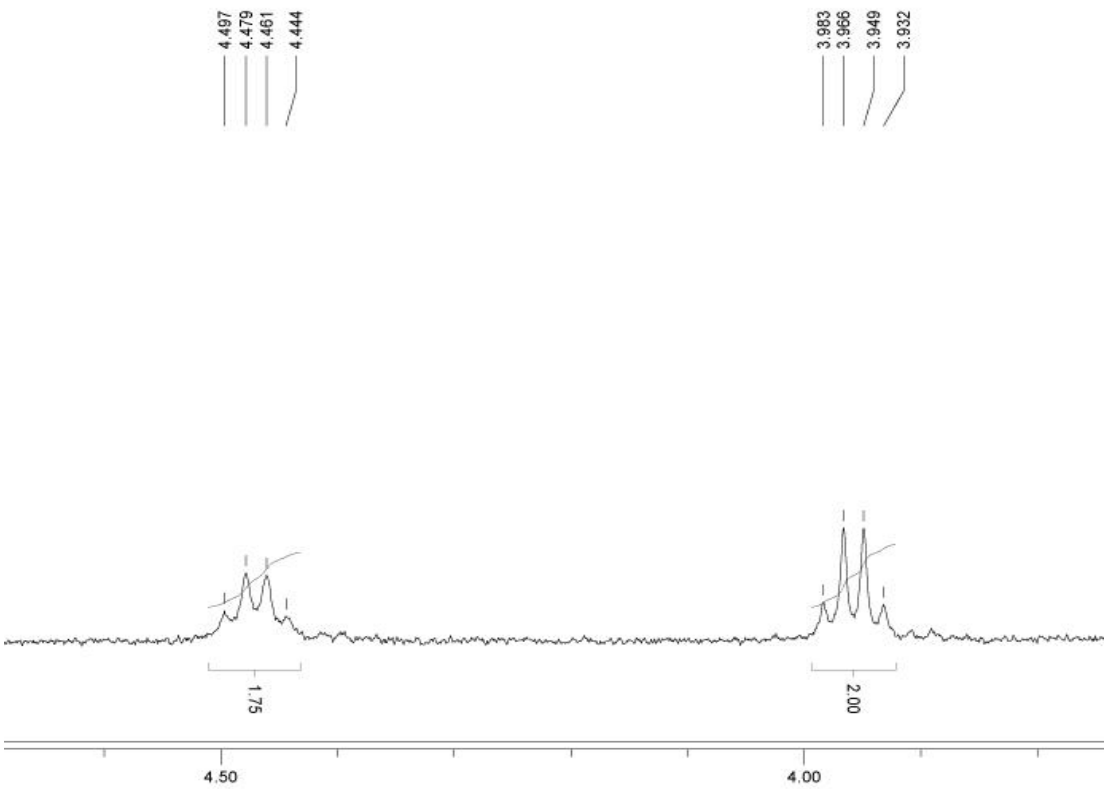


Fig. S1. ^{1}H NMR spectra of **6** measured immediately after its dissolution in d_6-DMSO.





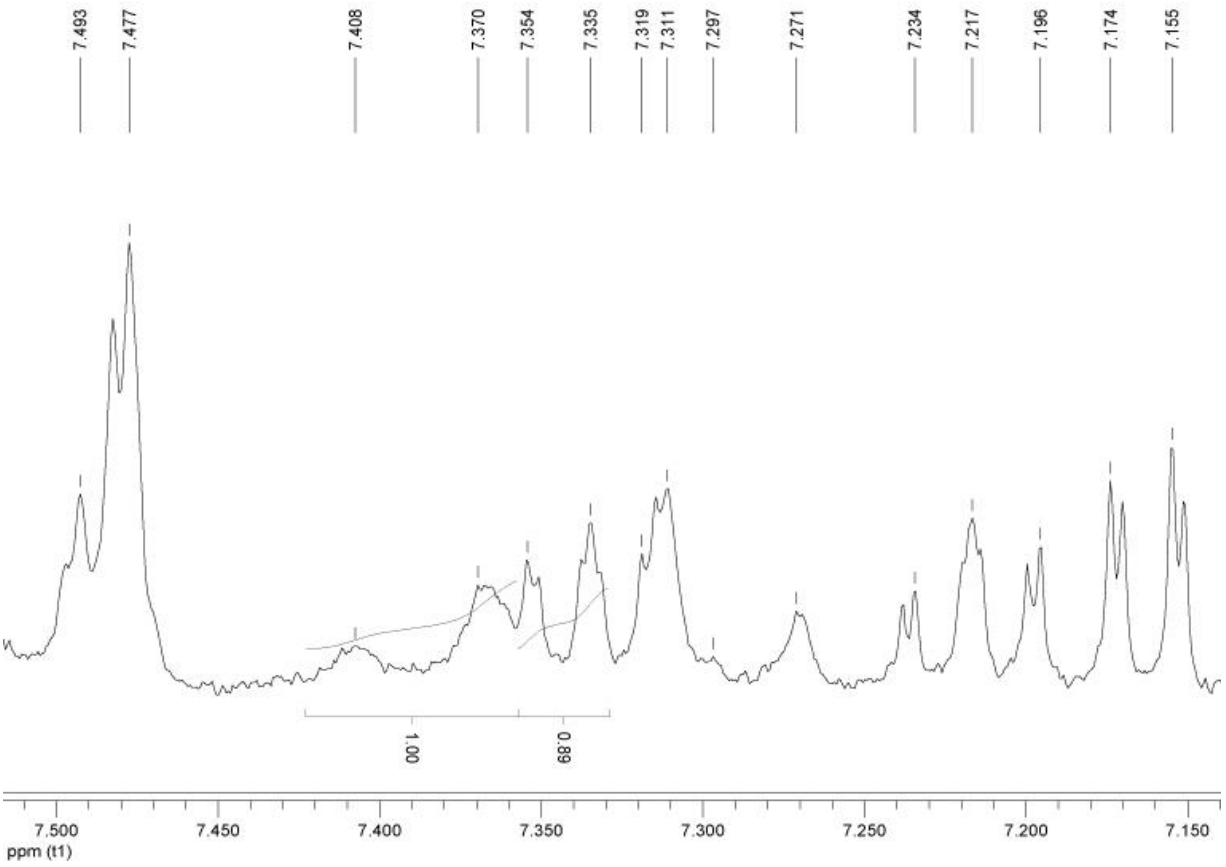


Fig. S2. ^{1}H NMR spectra of **6** measured 6 h later.

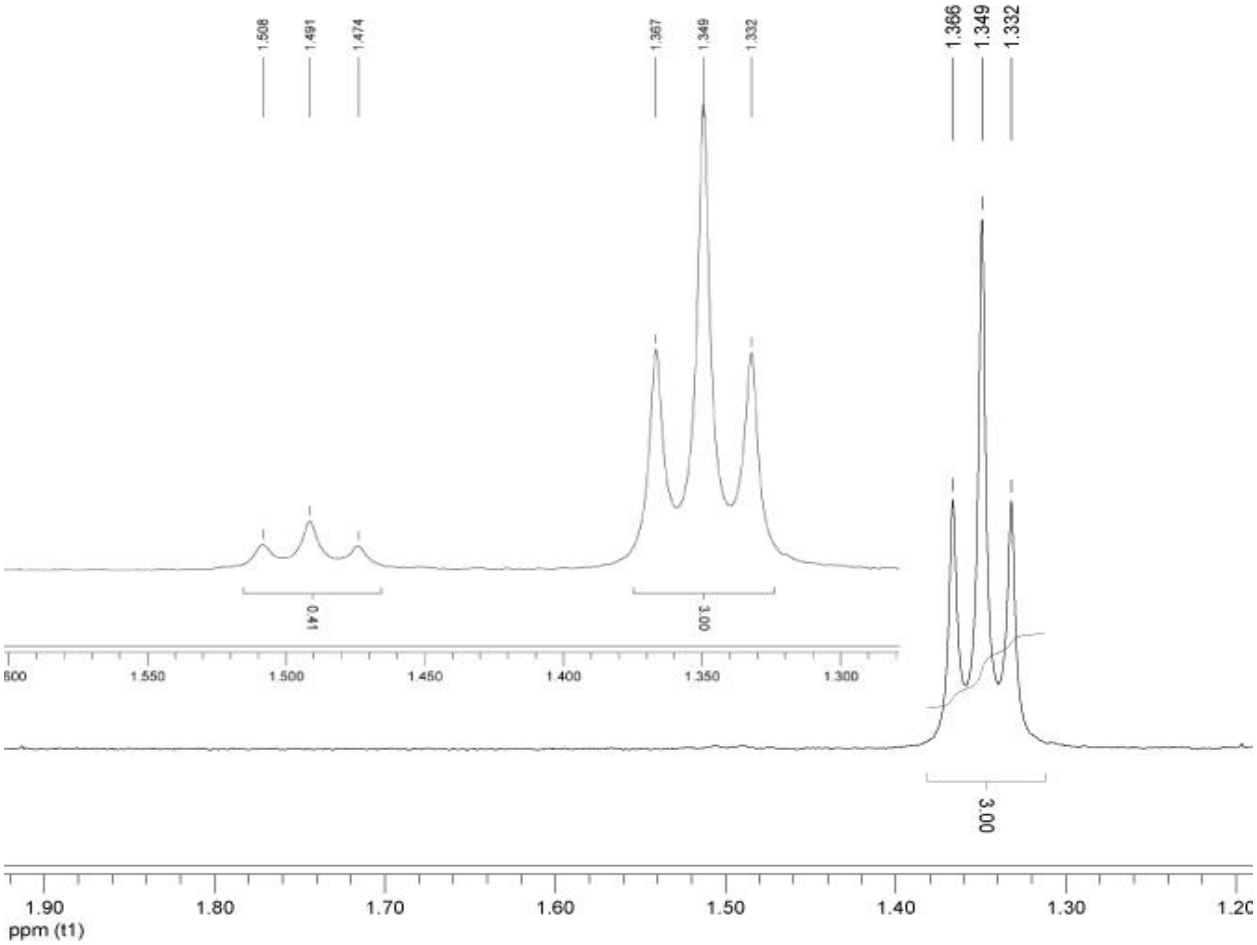
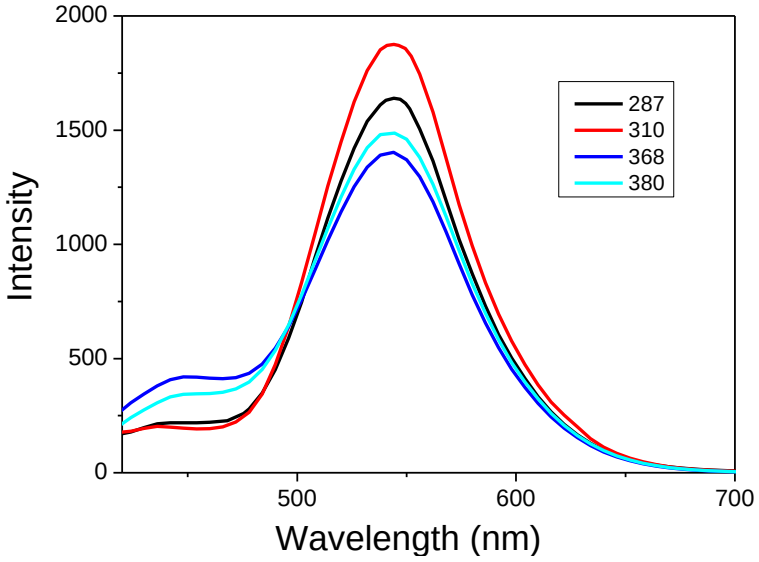
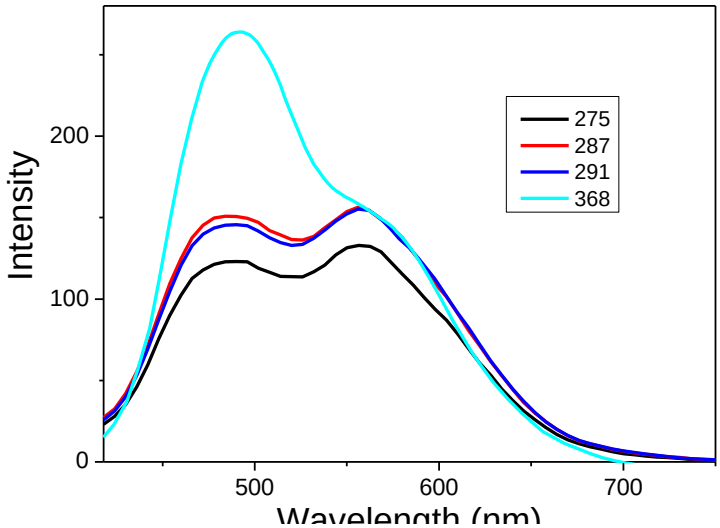


Fig. S3. ^{1}H NMR spectra of **2** measured immediately after its dissolution in d_6-DMSO, inset: measured 6 h later.



(a)



(b)

Fig. S4 Fluorescence emission spectra of **L** in THF (a) and DMF (b), inset: the excitation wavelengths.

Table S1. Crystallographic Data for complexes **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{75}H_{58}Cl_4N_8O_8S_2Cd$	$C_{75}H_{58}Cl_4N_8O_8S_2Zn$	$C_{74}H_{56}Cl_2N_8O_8S_2Co$	$C_{75}H_{58}Cl_4N_8O_8S_2Cu$	$C_{75}H_{58}Cl_4N_8O_8S_2Mn$	$C_{37}H_{28}N_4I_2SCd$
Formula Wt	1517.65	1470.58	1379.23	1468.75	1460.16	926.89
Crystal Syst	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	14.071(5)	13.9221(3)	11.0672(7)	13.8465(4)	14.0610(3)	19.953(5)
b (Å)	14.174(5)	14.1176(3)	15.9039(9)	14.0872(4)	14.1018(3)	13.943(5)
c (Å)	19.754(5)	20.0140(4)	19.6022(12)	20.0791(9)	19.9266(7)	27.347(5)
a (°)	97.391(5)	105.3220(10)	105.422(4)	105.473(3)	104.860(2)	90.000(5)
β (°)	103.966(5)	97.9320(10)	100.550(4)	98.160(3)	97.678(2)	106.629(5)
γ (°)	113.288(5)	112.5160(10)	94.827(4)	112.461(2)	112.8040(10)	90.000(5)
V [Å^3]	3399.1(19)	3376.01(12)	3237.5(3)	3355.0(2)	3397.99(16)	7290(3)
Z	2	2	2	2	4	4
D_c [g·cm^{-3}]	1.453	1.447	1.417	1.454	1.427	1.689
F(000)	1528	1516	1430	1514	1506	3584
Crystal Size (mm)	0.50×0.30×0.20	0.34×0.18×0.10	0.44×0.14×0.05	0.40×0.21×0.06	0.50×0.22×0.20	0.16×0.11×0.04
Temperature (K)	298(2)	296(2)	296(2)	296(2)	296(2)	298(2)
Radiation [Å] MoKα	0.71069	0.71073	0.71073	0.71073	0.71073	0.71069
N_{ref}, N_{par}	15486, 885	15371, 883	14843, 856	15439, 883	15562, 883	8087, 407
R_1, wR_2	0.0752, 0.1787	0.0667, 0.1865	0.0801, 0.1881	0.0716, 0.1896	0.0723, 0.2106	0.0878, 0.2230
Goodness-of-fit on F^2	1.008	1.046	1.016	1.050	1.060	1.025

Table S2. Selected bond lengths [Å] and angles [°] for **1–6**.

1		**2**		**3**		**4**		**5**		**6**	
Bond	lengths										
Cd1–N1	2.286(5)	Zn1–N1	2.082(3)	Co1–N1	2.057(4)	Cu1–N1	2.234(4)	Mn1–N1	2.271(3)	Cd1–N2	2.331(10)
Cd1–N2	2.328(6)	Zn1–N2	2.185(3)	Co1–N2	1.891(4)	Cu1–N2	2.002(3)	Mn1–N2	2.188(3)	Cd1–N1	2.347(11)
Cd1–N3	2.350(6)	Zn1–N3	2.186(3)	Co1–N3	2.059(4)	Cu1–N3	2.240(4)	Mn1–N3	2.247(3)	Cd1–N3	2.379(11)
Cd1–N4	2.367(6)	Zn1–N4	2.216(3)	Co1–N4	2.103(4)	Cu1–N4	2.141(3)	Mn1–N4	2.248(3)	Cd1–I2	2.724(16)
Cd1–N5	2.289(5)	Zn1–N5	2.076(3)	Co1–N5	1.908(4)	Cu1–N5	1.959(3)	Mn1–N5	2.254(3)	Cd1–I1	2.741(17)
Cd1–N6	2.338(7)	Zn1–N6	2.201(3)	Co1–N6	2.108(4)	Cu1–N6	2.128(4)	Mn1–N6	2.194(3)		
Bond	angles										
N1–Cd1–N2	70.0(2)	N1–Zn1–N2	74.85(11)	N1–Co1–N2	79.92(15)	N1–Cu1–N2	76.62(13)	N1–Mn1–N2	71.80(10)	N2–Cd1–N1	69.2(3)
N5–Cd1–N6	70.4(2)	N5–Zn1–N6	106.28(11)	N5–Co1–N6	79.41(16)	N5–Cu1–N6	78.47(13)	N5–Mn1–N6	72.50(11)	N2–Cd1–N3	68.9(4)
N1–Cd1–N3	69.9(2)	N2–Zn1–N3	150.18(11)	N2–Co1–N3	80.12(15)	N2–Cu1–N3	76.11(12)	N2–Mn1–N3	72.50(10)	N1–Cd1–I2	99.3(3)
N5–Cd1–N4	69.9(2)	N5–Zn1–N4	74.94(11)	N5–Co1–N4	79.06(16)	N5–Cu1–N4	77.62(12)	N5–Mn1–N4	72.04(11)	N3–Cd1–I1	101.8(3)

Table S3. Non-covalent interactions in the choromophores **1–5**.

1		**2**		**3**		**4**		**5**	
H–bond									
O2···H36–C36	2.668	O1···H17–C17	2.426	O1···H46–C46	2.405	O1···H46–C46	2.520	O1···H73B–C73	2.630
O3···H9–C9	2.481	O1···H73–C73	2.526	O2···H36B–C36	2.608	O1···H49–C49	2.452	O2···H9–C9	2.531
O3···H12–C12	2.455	O3···H46–C46	2.446	O3···H49–C49	2.641	O1···H58–C58	2.709	O2···H12–C12	2.449
O3···H19–C19	2.463	O3···H49–C49	2.425	O5···H21–C21	2.476	O2···H12–C12	2.705	O2···H21–C21	2.525
O4···H38–C38	2.701	O3···H54–C54	2.569	O5···H38–C38	2.493	O4···H1–C1	2.493	O3···H36B–C36	2.407
O5···H36–C36	2.642	O4···H3–C3	2.652	O6···H18–C18	2.563	O5···H36B–C36	2.422	O3···H52–C52	2.510
O5···H40–C40	2.690	O4···H36–C36	2.628	O6···H73–C73	2.575	O5···H38–C38	2.521	O5···H14–C14	2.706
O8···H3–C3	2.708	O6···H51–C51	2.702	O7···H14–C14	2.715	O7···H4–C4	2.419	O6···H41–C41	2.419
O8···H59B–C59	2.621	O7···H9–C9	2.516	O7···H38–C38	2.664	O7···H7–C7	2.401	O6···H44–C44	2.474
O10···H1–C1	2.443	O7···H12–C12	2.439	O8···H12–C12	2.639	O7···H17–C17	2.563	O6···H54–C54	2.519
O10···H73B–C73	2.439	O7···H21–C21	2.626	O8···H13–C13	2.491	O8···H40–C40	2.711	O7···H15–C15	2.582
O11···H30–C30	2.613	O8···H52–C52	2.488			O8···H73B–C73	2.613		
O11···H33–C33	2.516	O8···H62–C62	2.709					*Cl2S···H52–C52*	*2.922*
O11···H39–C39	2.476	*O5···H1SA–C1S*	*2.499*	*S1···H44A–C44*	*2.908*	*O2···H1S1–C1S*	*2.441*	*O8···H1SA–C1S*	*2.640*
C–H···π									
a	2.810	a	2.756	a	2.818	a	2.777	a	2.772