Photochromic macrocyclic complexes of Yttrium(III) undergoing merocyanine to spiropyran isomerization as models for Single-Molecule Magnets switches candidates

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Electronic Supplementary Information

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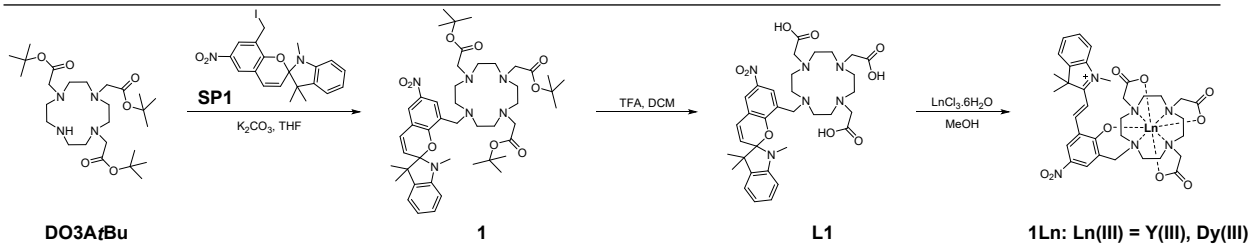
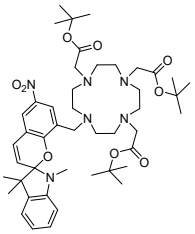
Materials and methods

Reagents were purchased from ACROS Organics and from Aldrich Chemical Co and used without further purification. DO3A*t*Bu was purchased from CheMatech and TCI Europe. All solvents were dried and distilled prior to use according to standard methods. All the experiments and purifications were carefully processed in the dark. Purifications by flash chromatography were performed on a grace-reveleris equipment and the columns were purchased from Interchim. Analytic HPLC was performed on a Prominence Shimadzu HPLC/LCMS-2020 equipped with a UV SPD-20 A detector. The chromatographic system employs HPLC (Vision HT C18 HL 5 µ 250× 4.6 mm) with H_2O and MeCN as eluents (gradient given under the chromatogram) at a flow rate of 1 mL/min and UV detection at 254, 350, and 360 nm. NMR spectra were recorded at the "Services communs" of the University of Brest and at the Institut des Sciences Chimiques de Rennes. ^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance 500 (500 MHz), Bruker Avance 400 (400 MHz), or BrukerAMX-3 300 (300 MHz) spectrometers. HRMS analyses were realized on a HRMS Q-Tof MaXis, sources ESI, APCI, APPI, nano-ESI (at the Institute of Organic and Analytic Chemistry – ICOA in Orléans and Centre Régional de Mesures Physiques de l'Ouest in Rennes). X-ray measurements were performed with a crystal mounted on a glass fiber with paratone oil on a Bruker APEX-II (D8 VENTURE Bruker AXS). Absorption measurements were performed in methanol, dichloromethane, and acetonitrile at room temperature using "UV VIS NIR JASCO" spectrometer. Routine UV-vis irradiations were performed in UV cells with a Xenon lamp (with a filter at λ = 380, 450, and 530 nm).

Synthetic procedures and characterization



*Scheme S1 : Synthesis of complexes **1Ln.***



Synthesis of compound 1 (adapted from reference[1]): A solution of **DO3A*t*Bu** (37 mg, 73 µmol) and K_2CO_3 (30 mg, 218 µmol, 3 equiv) in THF (3.2 mL) was stirred at room temperature for 30 min. To this solution was added dropwise a solution of the spiropyran **SP1**[2] (37 mg, 80 µmol, 1.1 equiv) in THF (1 mL). The reaction mixture was stirred under reflux for 24h. The K_2CO_3 salts were filtered on cotton and solvents were evaporated to dryness. The residue was then submitted to a chromatography on silica gel (Eluent: CH_2Cl_2/MeOH 1001/1 to 100/3) to give compound **1** (36 mg, 42 µmol, y = 58%) as a pink/red oil.

- ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H, H2), 7.93 (d, *J* = 2.7 Hz, 1H, H4), 7.17 (td, *J* = 7.7, 1.1 Hz, 1H, H14), 7.04 (d, *J* = 6.8 Hz, 1H, H12), 6.95 (d, *J* = 10.4 Hz, 1H, H7), 6.86 (dd, *J* = 10.9, 3.9 Hz, 1H, H13), 6.50 (d, *J* = 7.7 Hz, 1H, H15), 5.87 (d, *J* = 10.3 Hz, 1H, H8), 3.58 (d, *J* = 13.2 Hz, 1H, H17a), 3.43 (d, *J* = 15.0 Hz, 1H, H17b), from 3.12 to 2.01, 22H, cyclen and 3 *CH_2COOCH$_3$), 2.70 (s, 3H, N-CH$_3$), 1.49 (s, 9H, *t*Bu), 1.42-1.41 (2s, 18H, *t*Bu), 1.23 (s, 3H, CH$_3$ gem), 1.16 (s, 3H, CH$_3$ gem).
- ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.7 (C=O), 173.5 (C=O), 172.7 (C=O), 158.4 (C5), 147.2 (C16), 140.4 (C3), 135.6 (c11), 128.8 (C7), 128.1 (C2, C14), 123.4 (C1), 122.2 (4), 121.5 (C8, C12), 119.9 (C13), 119.1 (C6), 107.6 (C9), 106.9 (C15), 82.9 (Cq *t*Bu), 82.7 (Cq *t*Bu), 82.3 (Cq *t*Bu), 56.9 and 55.8 ($\underline{CH_2}$COOCH$_3$ + cyclen), 52.3 (C10), 50.5 (C17), 28.9 (NCH$_3$), 27.9 (*t*Bu), 27.8 (*t*Bu), 25.9 (CH$_3$ gem), 20.0 (CH$_3$ gem).
- ESI-HR-MS (positive, MeOH): *m/z* calcd. for $[C_{46}H_{68}N_6NaO_9]^+$: 871.4939, found: 871.4924, $[M+Na]^+$; calcd. for $[C_{46}H_{69}N_6O_9]^+$: 849.5120, found: 849.5109, $[M+H]^+$; calcd. for $[C_{46}H_{70}N_6O_9]^{2+}$: 425.2597, found: 425.2595, $[M+2H]^{2+}$, 335 and 515 = fragmentation (-O*t*Bu).

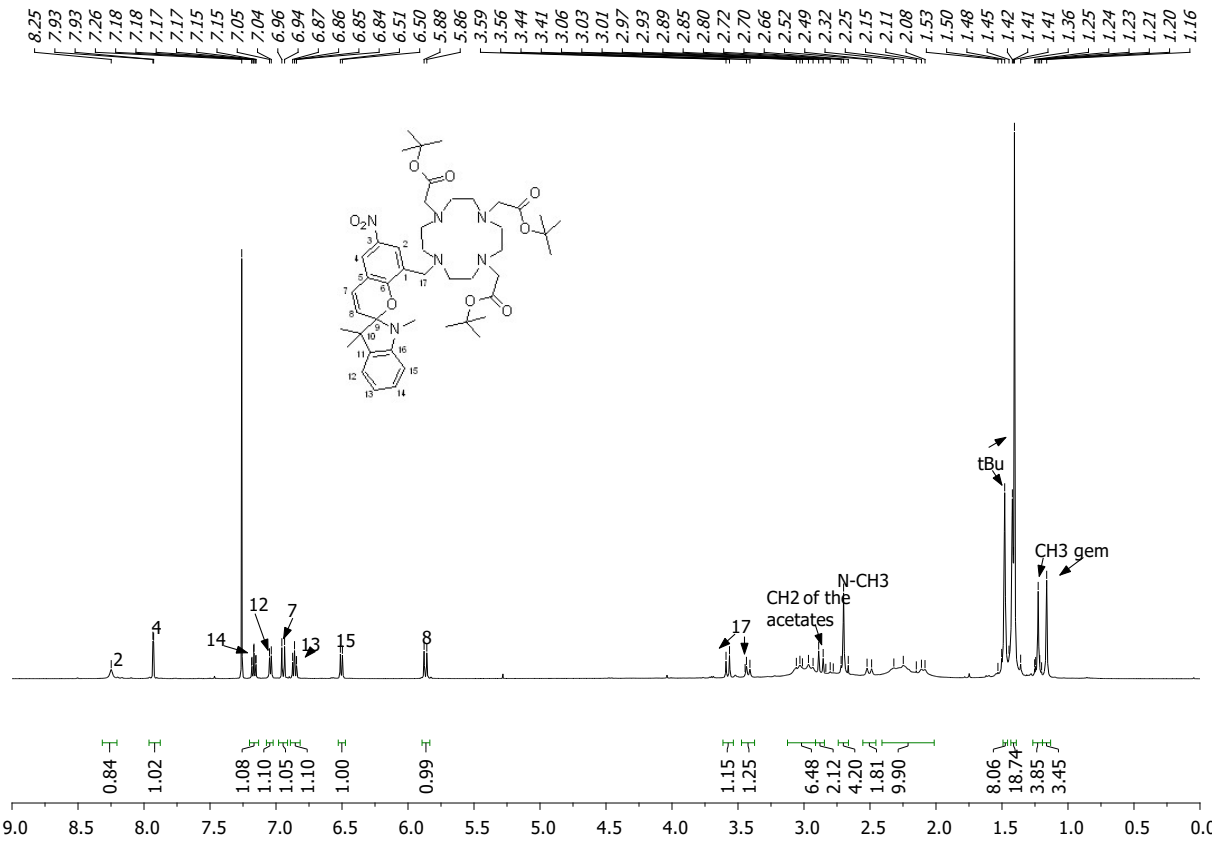


*Figure S1 : ^{1}H NMR of compound **1** (500 MHz, $CDCl_3$, 298K).*

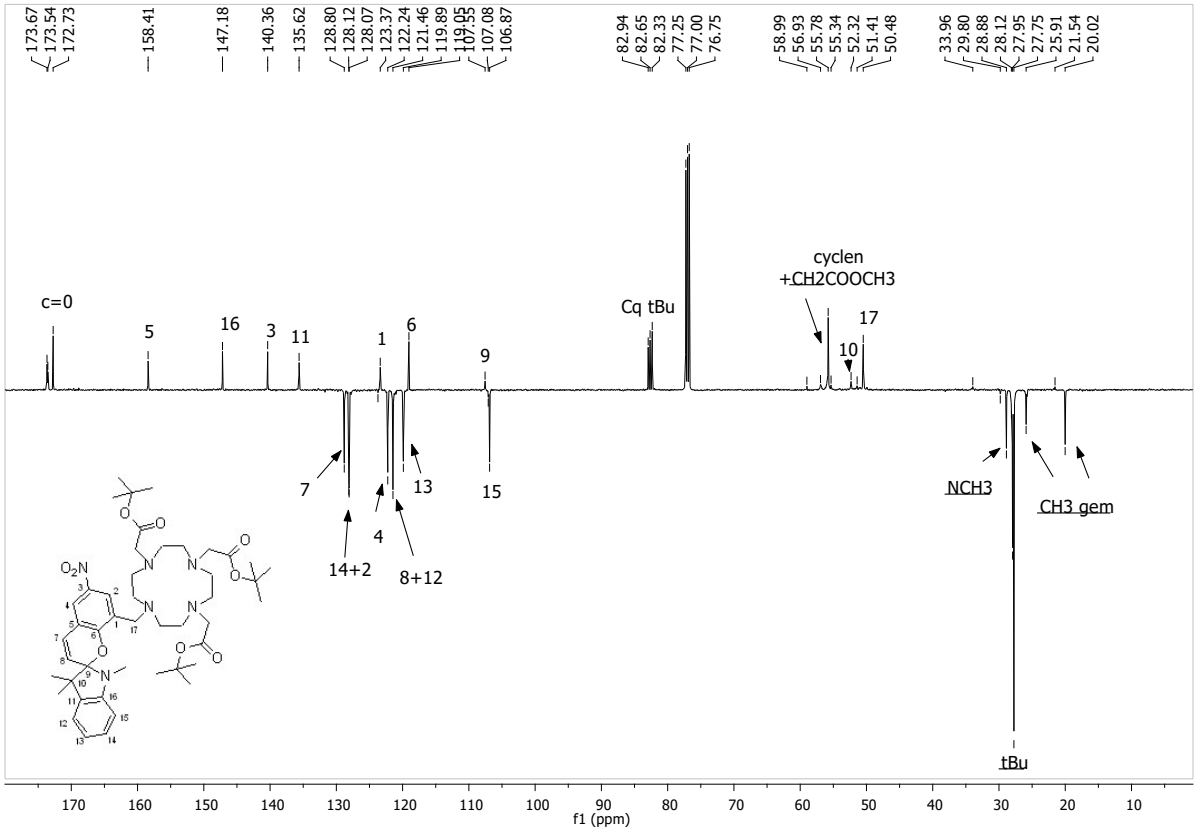
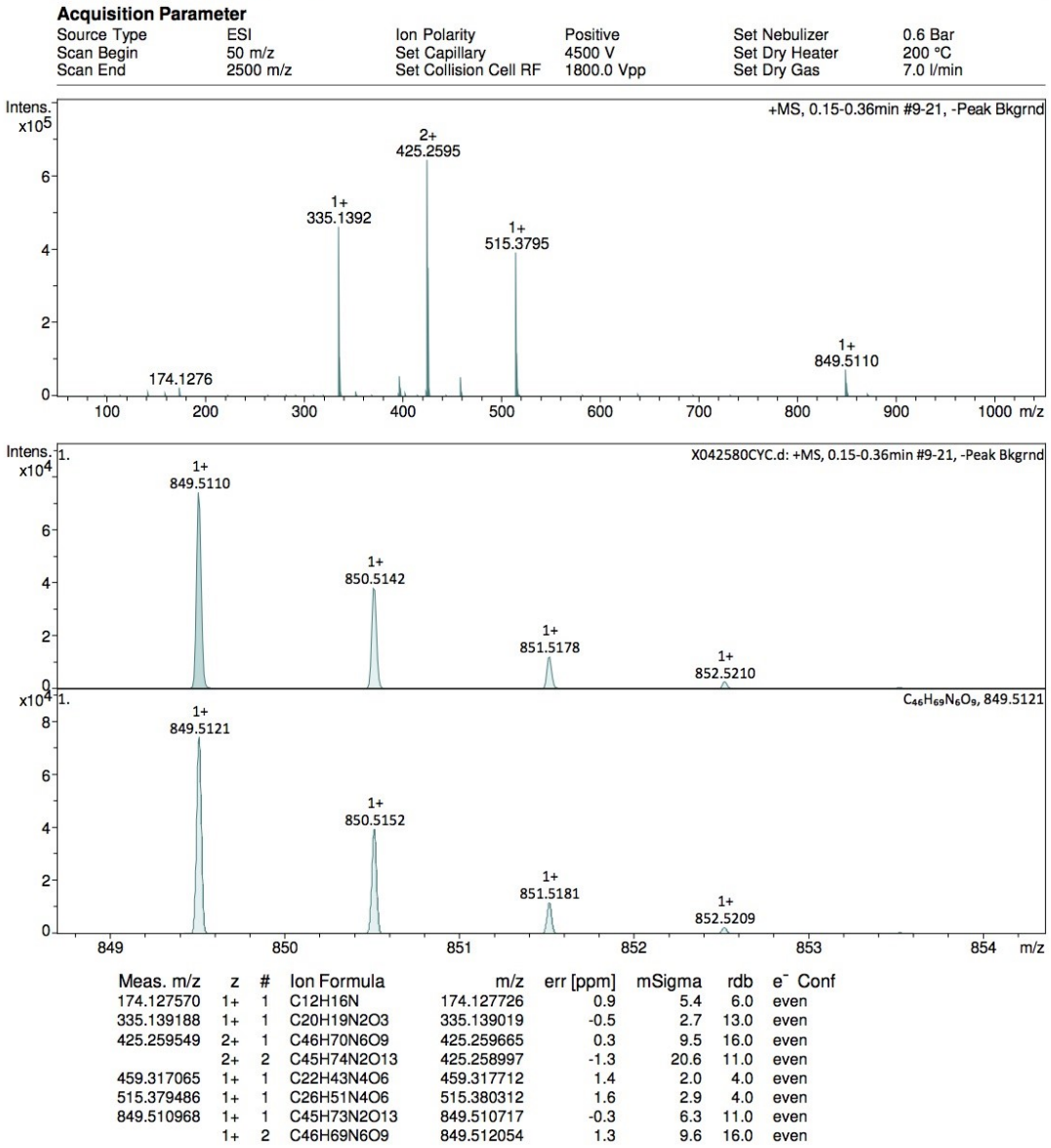
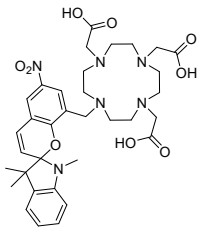


*Figure S2: ^{13}C NMR of compound **1** (125 MHz, $CDCl_3$, 298K).*



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e⁻ Conf
174.127570	1+	1	C12H16N	174.127726	0.9	5.4	6.0	even
335.139188	1+	1	C20H19N2O3	335.139019	-0.5	2.7	13.0	even
425.259549	2+	1	C46H70N6O9	425.259665	0.3	9.5	16.0	even
	2+	2	C45H74N2O13	425.258997	-1.3	20.6	11.0	even
459.317065	1+	1	C22H43N4O6	459.317712	1.4	2.0	4.0	even
515.379486	1+	1	C26H51N4O6	515.380312	1.6	2.9	4.0	even
849.510968	1+	1	C45H73N2O13	849.510717	-0.3	6.3	11.0	even
	1+	2	C46H69N6O9	849.512054	1.3	9.6	16.0	even

*Figure S3: HRMS of compound **1**.*



Synthesis of L1: To a solution of compound **1** (100 mg, 0.12 mmol) in CH_2Cl_2 (2.14 mL) was added dropwise TFA (2.14 mL). The reaction mixture was stirred at 40°C for 4 hours and solvents were evaporated to dryness. The residue was dissolved in methanol and solvents were evaporated to dryness. The process was repeated three times. The residue was purified by flash column chromatography on C18-silica gel (Column C18-4g from Interchim, Eluent: H_2O/ACN 95/5 for 10 min,

then H_2O/ACN 95/5 to 2/8 for 30 min, flow: 15 mL/min) to give compound **L1** (90 mg) as a red oil. Compound **L1** was then used without further purification in the next step.

- ^1H NMR (CD_3OD, 300 MHz): Because of the quick isomerization process, the ^1H NMR spectrum was obtained as a mixture of isomers. Therefore, due to its complexity, the spectrum could not be described but is given below. Because of the complexity of the ^1H NMR spectrum, no ^{13}C NMR was attempted.
- ESI-HR-MS (positive, MeOH): *m/z* calcd. for $[C_{34}H_{45}N_6O_9]^+$: 681.3243, found: 681.3229, $[M+H]^+$; calcd. for $[C_{34}H_{42}FeN_6O_9]^+$: 734.2357, found: 734.2346, $[M-2H+Fe]^+$; calcd. for $[C_{34}H_{46}N_6O_9]^{2+}$: 341.1658, found: 341.1658, $[M+2H]^{2+}$; calcd. for $[C_{34}H_{43}FeN_6O_9]^{2+}$: 367.6215, found: 367.6214, $[M-H+Fe]^{2+}$,335 and 347 = fragmentations.

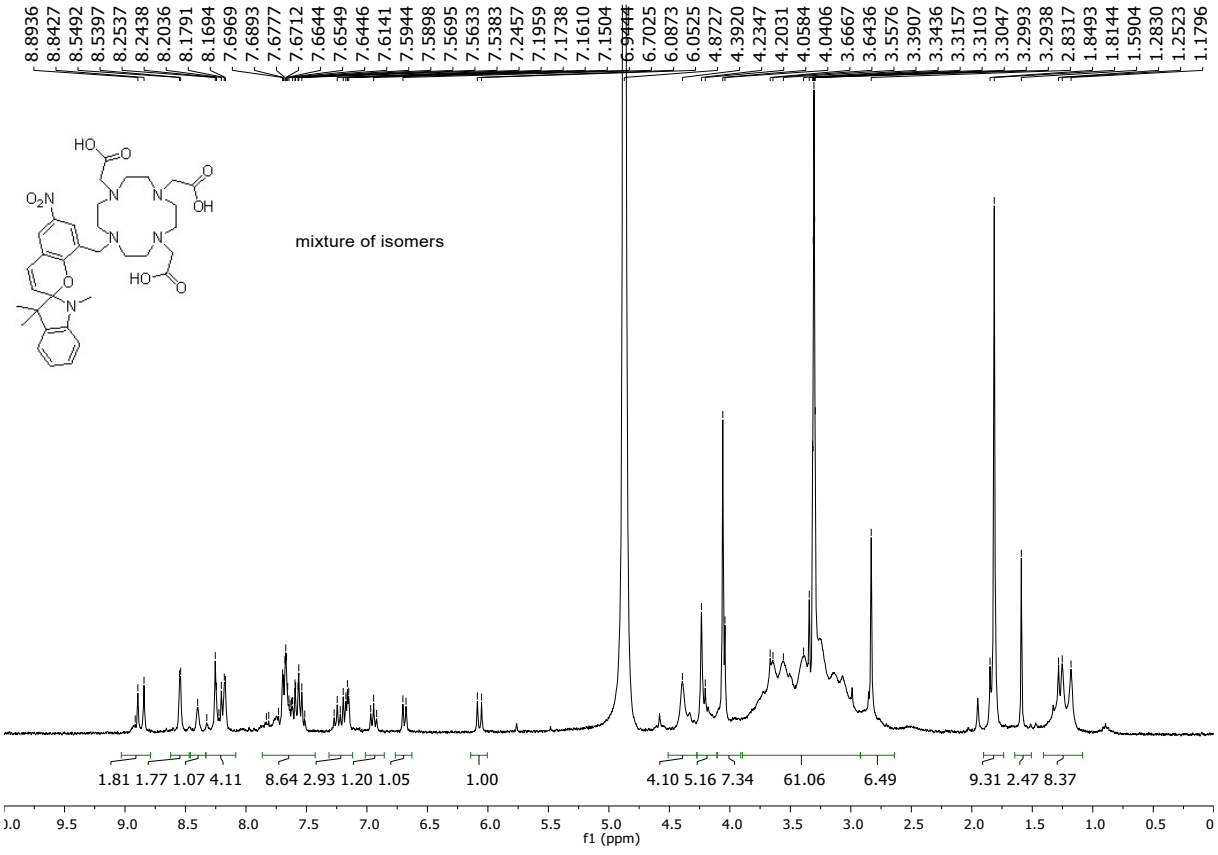
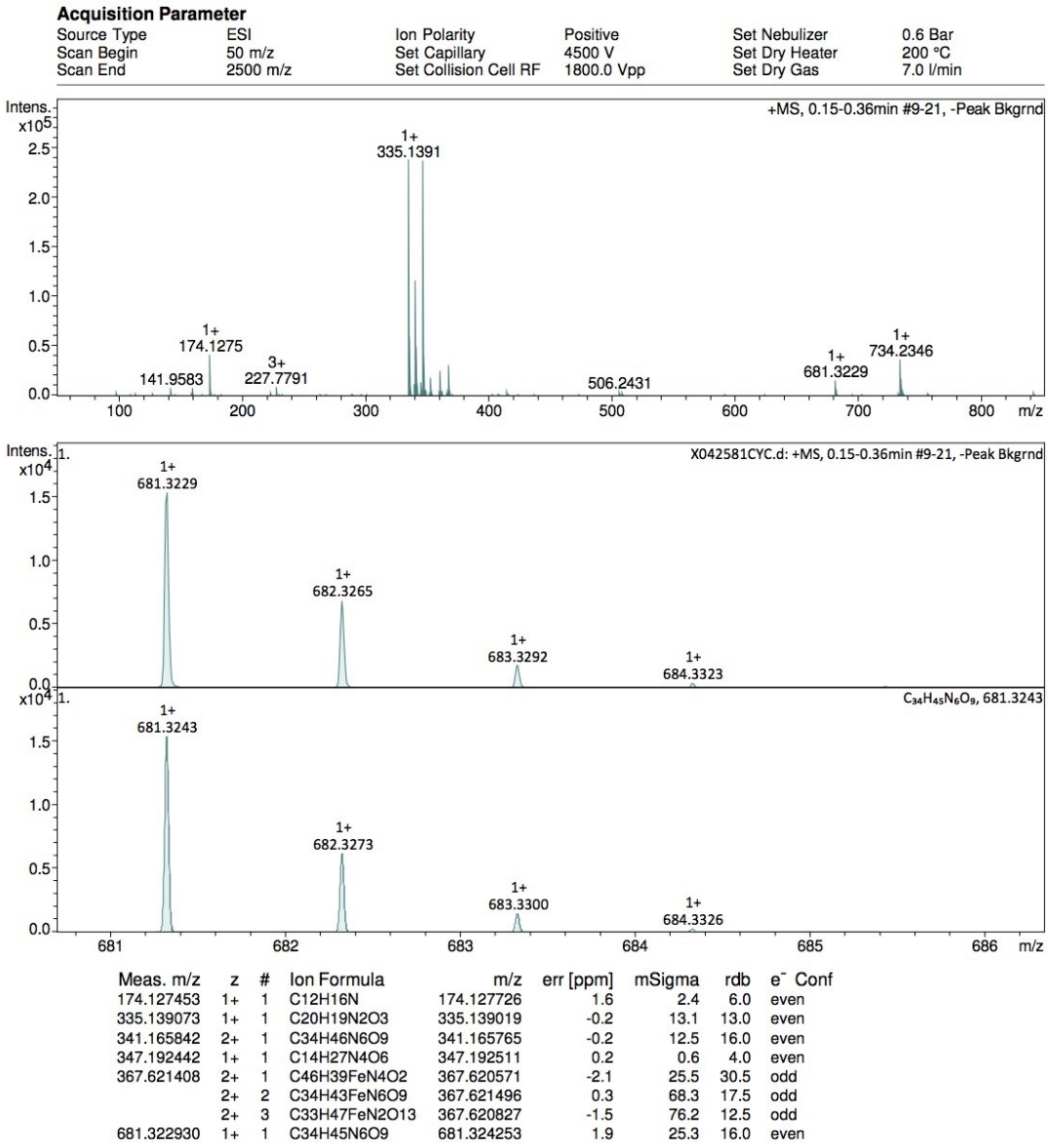
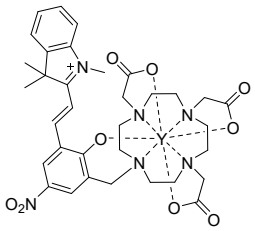


*Figure S4: ^1H NMR (D_2O, 300 MHz, 298 K) of compound L**1**.*



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e⁻ Conf
174.127453	1+	1	C12H16N	174.127726	1.6	2.4	6.0	even
335.139073	1+	1	C20H19N2O3	335.139019	-0.2	13.1	13.0	even
341.165842	2+	1	C34H46N6O9	341.165765	-0.2	12.5	16.0	even
347.192442	1+	1	C14H27N4O6	347.192511	0.2	0.6	4.0	even
367.621408	2+	1	C46H39FeN4O2	367.620571	-2.1	25.5	30.5	odd
	2+	2	C34H43FeN6O9	367.621496	0.3	68.3	17.5	odd
	2+	3	C33H47FeN2O13	367.620827	-1.5	76.2	12.5	odd
681.322930	1+	1	C34H45N6O9	681.324253	1.9	25.3	16.0	even

*Figure S5: HRMS of compound **L1***



Synthesis of 1Y: To a solution of **L1** (32 mg, 47 µmol), in MeOH (10 mL) was added $YCl_3.6H_2O$ (43 mg, 141 µmol, 3 equiv). The reaction mixture was stirred at room temperature for 2.5 days before evaporation of solvents to dryness. Purification of the crude by flash chromatography on C18-silica gel (Column C18-4g from Interchim, Eluent: H_2O/ACN 95/5 for 10 min, then H_2O/ACN 95/5 to 2/8 for 30 min, flow: 15 mL/min) gave **1Y** (31 mg, 40 µmol, y = 86%) as a red dry film of amorphous solid.

- ESI-HR-MS (positive, MeOH): *m/z* calcd. for $[C_{34}H_{42}N_6O_9Y]^+$: 767.2066, found: 767.2060, $[M+H]^+$; calcd. for $[C_{34}H_{43}N_6O_9Y]^{2+}$: 384.1069, found: 384.1065, $[M+2H]^{2+}$.
- ^{1}H NMR (500 MHz, CD_3OD): δ 8.63 (d, *J* = 3.0 Hz, 1H), 8.61 (bd, 1H, this signal tends to disappear upon standing in CD_3OD under 450 nm irradiation), 8.25 (d, *J* = 15.9 Hz, 1H, this signal transforms into a singlet upon standing in CD_3OD under 450 nm irradiation), 8.19 (d, *J* = 3.0 Hz, 1H), 7.76 (d, *J* = 7.1 Hz, 1H), 7.72 (d, *J* = 7.1 Hz, 1H), 7.60 (m, 2H), 4.27 (s, 3H), 3.8-2.2(m, 24H), 1.83 (m, 6H).

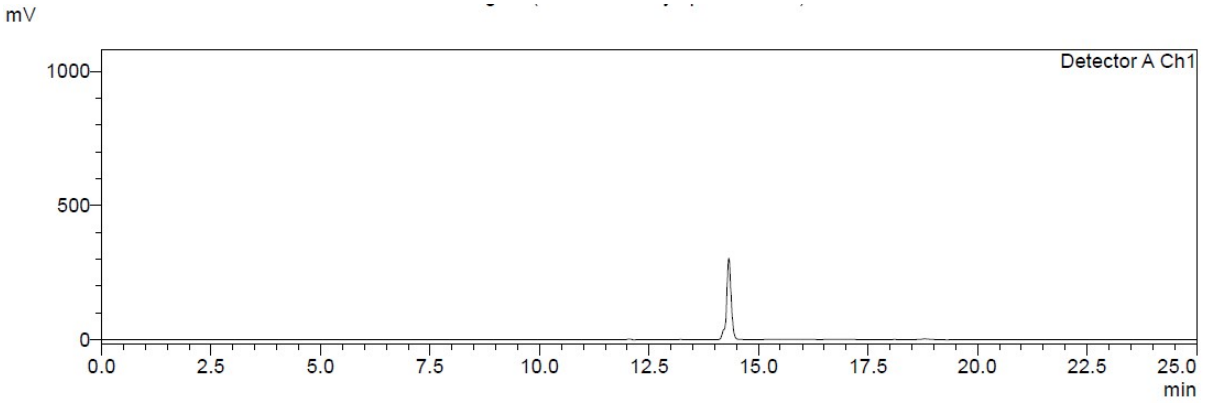


*Figure S6: Analytical HPLC of the **1Y** complex. Column: Vision HT C18 HL 5 µ 250× 4.6 mm. Gradient: 100% H_2O 0→5 min, 0→90% ACN 5-15 min, 90% ACN 15→20 min, 100% H_2O 20→25min. Flow: 1mL/min. Retention time = 14.332 min. Purity = 98%.*

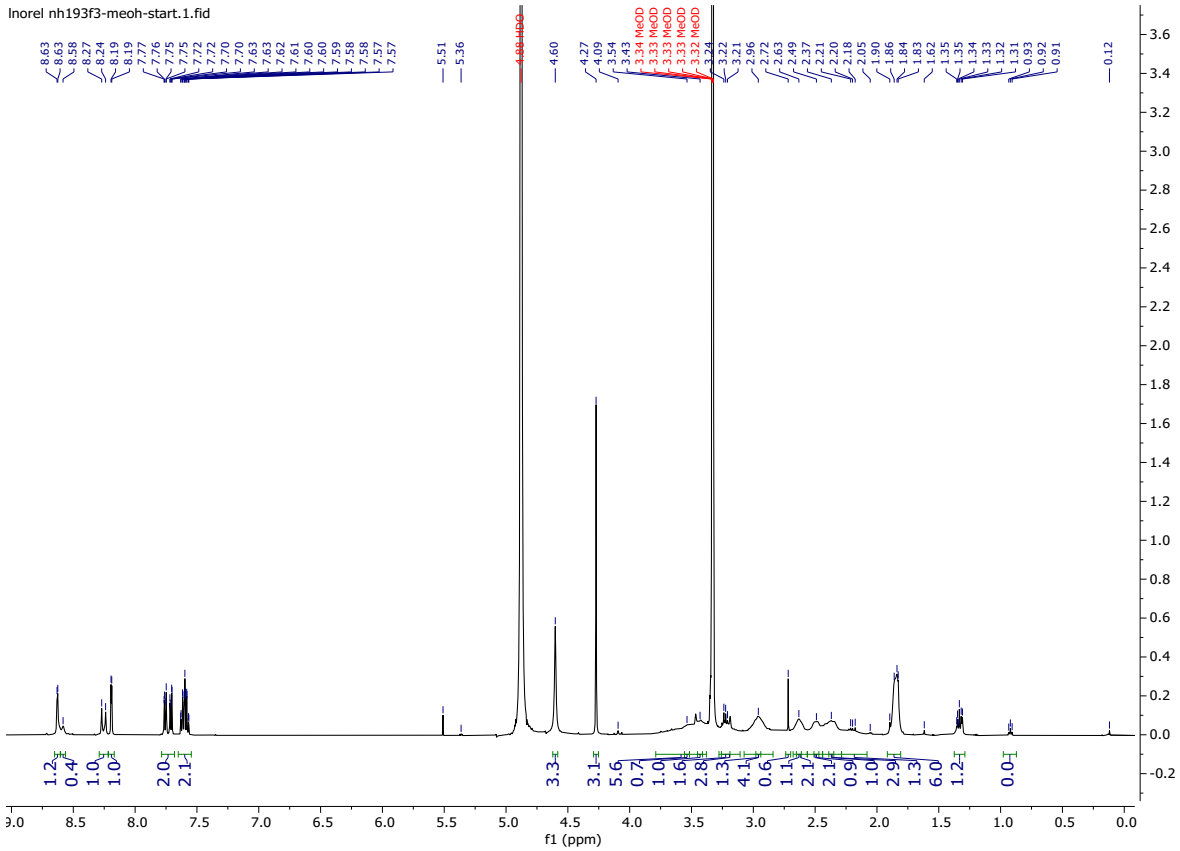
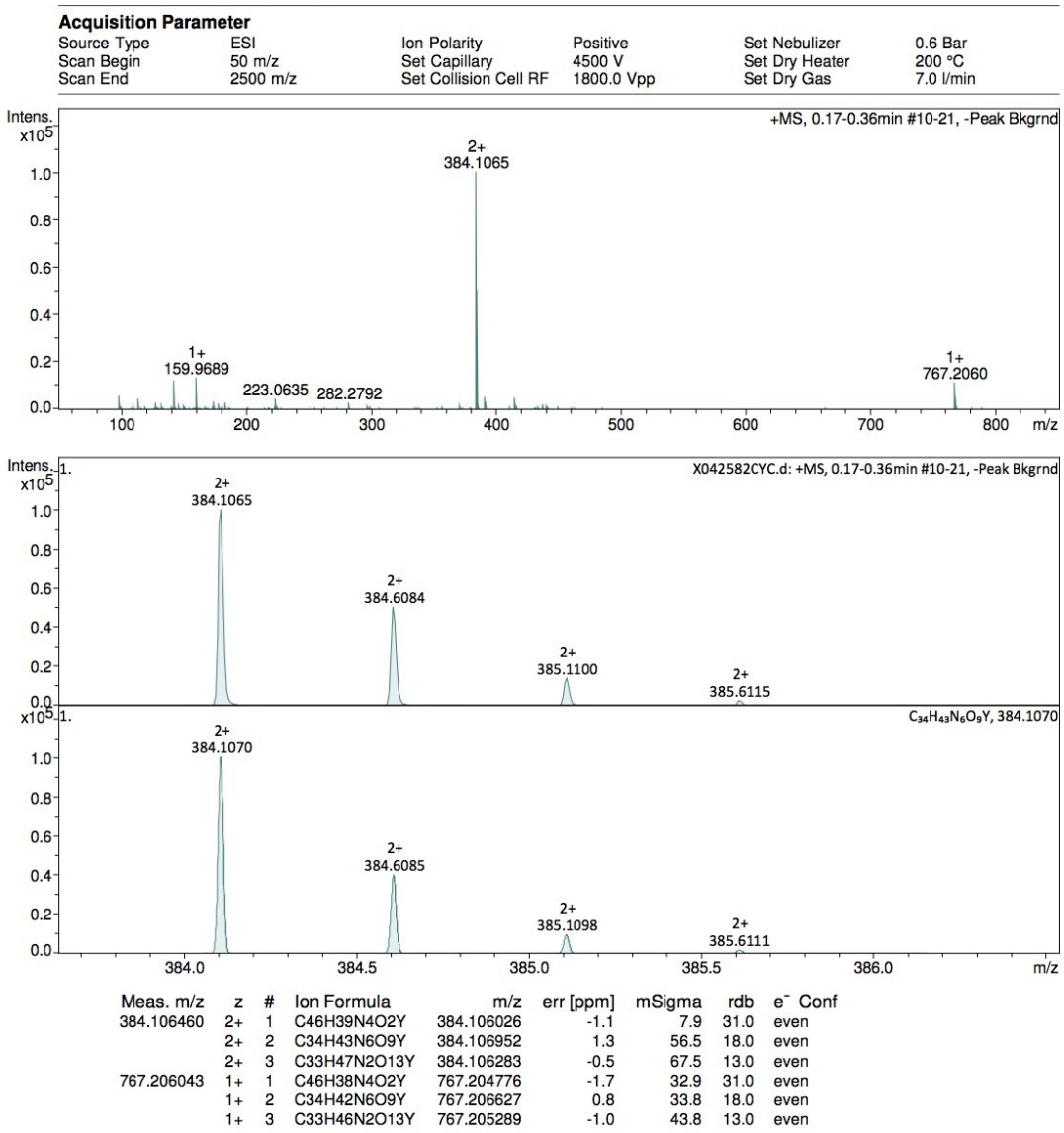
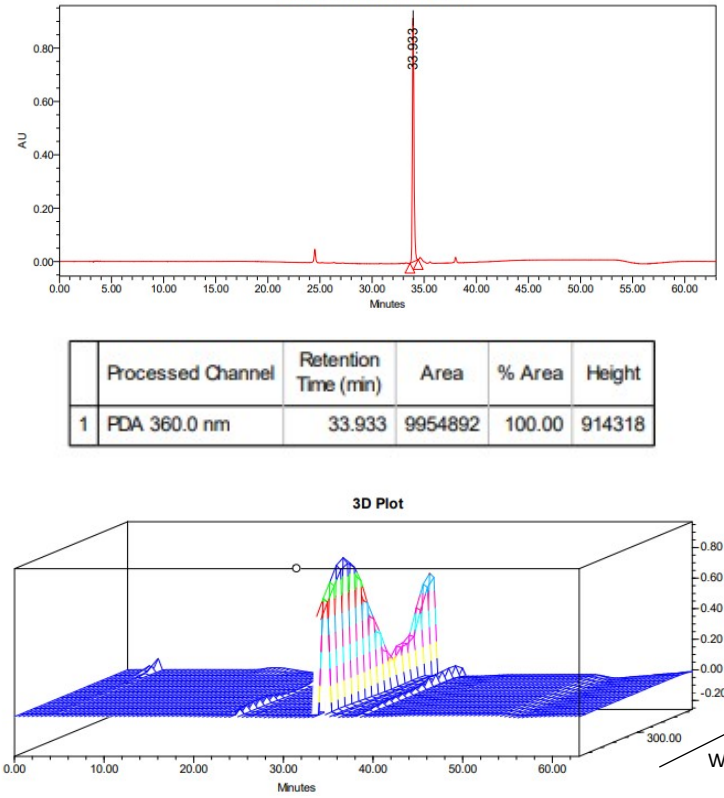


*Figure S7: [1]H NMR (CD_3OD, 500 MHz, 298 K) of compound **1Y**.*



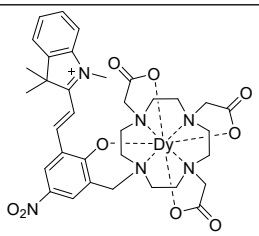
Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e⁻ Conf
384.106460	2+	1	C46H39N4O2Y	384.106026	-1.1	7.9	31.0	even
	2+	2	C34H43N6O9Y	384.106952	1.3	56.5	18.0	even
	2+	3	C33H47N2O13Y	384.106283	-0.5	67.5	13.0	even
767.206043	1+	1	C46H38N4O2Y	767.204776	-1.7	32.9	31.0	even
	1+	2	C34H42N6O9Y	767.206627	0.8	33.8	18.0	even
	1+	3	C33H46N2O13Y	767.205289	-1.0	43.8	13.0	even

*Figure S8: HRMS of compound **1Y.***



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 360.0 nm	33.933	9954892	100.00	914318

*Figure S9: HPLC-UV-DAD analysis of compound **1Y**. Column: MODULO-CART QS UPTISPHERE 5 ODB 250x 4.6 mmUP50DB-25QS. Gradient: 5% MeOH – 95 % H_2O. Injection volume 20.00 ul. λ = 360 nm. Retention time = 33.933 min, purity = 92 %.*



Synthesis of 1Dy: To a solution of $\mathbf{L_1}$ (59 mg, 87 µmol), in MeOH (10 mL) was added $DyCl_3.6H_2O$ (49 mg, 130 µmol, 1.5 equiv). The reaction mixture was stirred at room temperature for 4 days before evaporation of solvents to dryness. Purification of the crude by flash chromatography on C18-silica gel (Column C18-4g from Interchim, Eluent: H_2O for 10 min, H_2O/ACN 100/0 to 0/100 for 30 min, 100% ACN for 10 min, flow: 10 mL/min) gave **1Dy** (49 mg, 58 µmol, y = 68%) as an orange dry film of amorphous solid.

- ESI-HR-MS (positive, MeOH): *m/z* calcd. for $[C_{34}H_{43}DyN_6O_9]^+$: 421.6186 , found: 421.6192 , $[M+2H]^{2}+$; calcd. for $[C_{34}H_{42}DyN_6O_9]^+$: 842.2299 , found: 842.2315, $[M+H]^+$; m/z 174 = fragmentation.

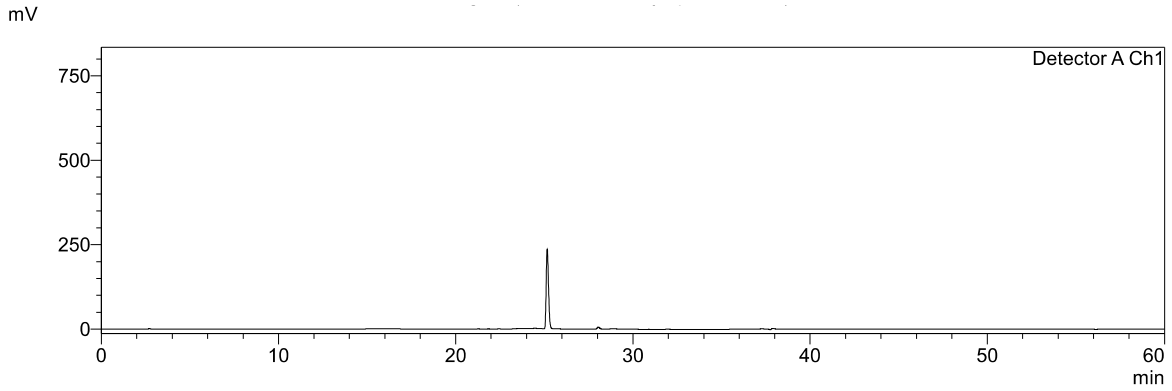
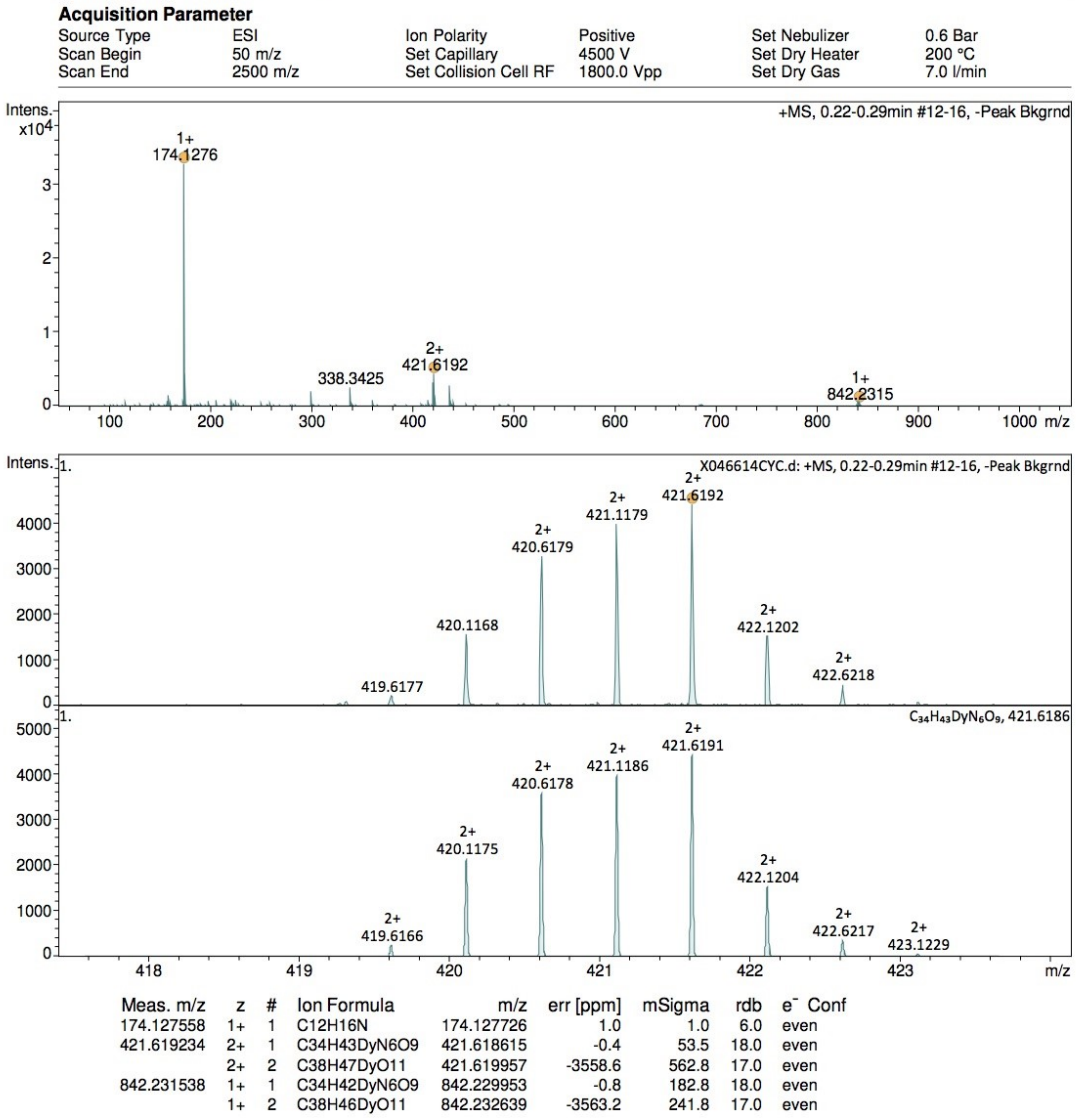
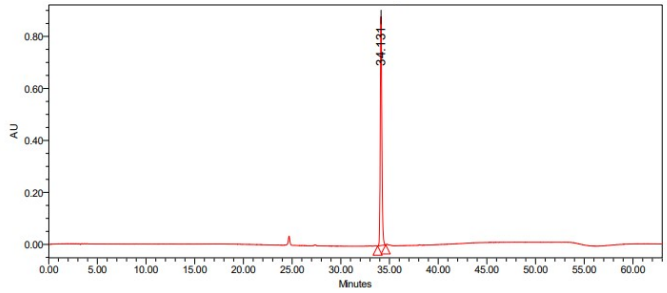


*Figure S10: Analytical HPLC of the **1Dy** complex. Column: Vision HT C18 HL 5 µ 250× 4.6 mm. Gradient: H_2O/ACN 98/2 0→8 min, 2→80% ACN 8→38 min, 80% ACN 38→48 min, 80→2% ACN 48→53 min, H_2O/ACN 98/2 53→63 min. Flow: 1mL/min. Retention time = 25.163 min, purity = 95%.*



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e⁻ Conf
174.127558	1+	1	C12H16N	174.127726	1.0	1.0	6.0	even
421.619234	2+	1	C34H43DyN6O9	421.618615	-0.4	53.5	18.0	even
	2+	2	C38H47DyO11	421.619957	-3558.6	562.8	17.0	even
842.231538	1+	1	C34H42DyN6O9	842.229953	-0.8	182.8	18.0	even
	1+	2	C38H46DyO11	842.232639	-3563.2	241.8	17.0	even

*Figure S11: HRMS of compound **1Dy**.*



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 360.0 nm	34.131	9861755	100.00	880235

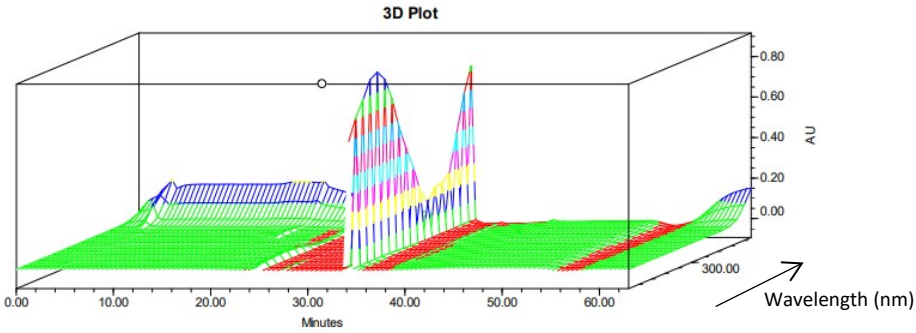
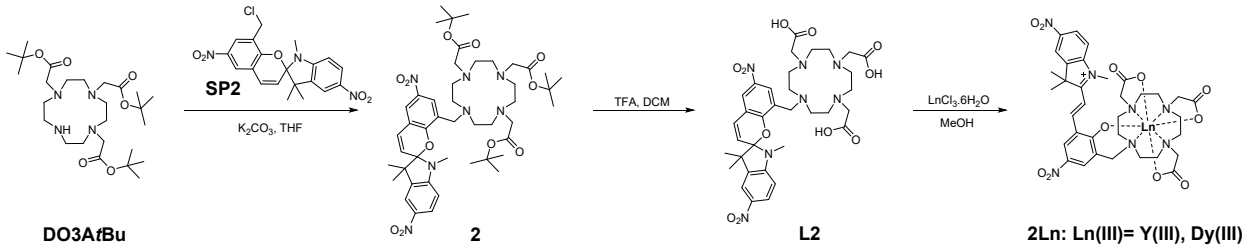
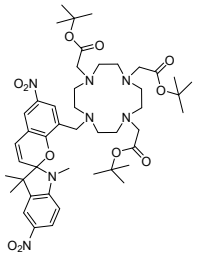


*Figure S12: HPLC-UV-DAD analysis of compound **1Dy**. Column: MODULO-CART QS UPTISPHERE 5 ODB 250x 4.6 mmUP50DB-25QS. Gradient: 5% MeOH – 95 % H_2O. Injection volume 20.00 ul. λ = 360 nm. Retention time = 34.131 min, purity = 92 %.*



*Scheme S2 : Synthesis of complexes **2Ln.***



Synthesis of 2: Compound **2** was prepared following literature procedure but starting with the chloro substituted **SP2** rather than from the iodo- one.[3] A solution of commercially available tri-*tert*-butyl

2,2',2''-(1,4,7,10-tetraazacyclododecane-1,4,7-triyl)triacetate (0.225 g, 0.437 mmol, 1 eq) and dry potassium carbonate (0.181 g, 1.31 mmol, 3 eq) in 19 mL of dry THF was stirred in a round bottom flask under argon for 30 min. A solution of compound **SP2** (0.20 g, 0.481 mmol) in 6 mL of dry THF was introduced to the flask dropwise. The mixture was refluxed overnight under inert atmosphere. After cooling to room temperature, the solution was filtered over a pad of cotton to remove the residual salt. The solvent was removed by the rotary evaporator. The crude product was purified over silica column chromatography with dichloromethane: methanol (100:0 to 93:7%) as eluent. Compound **2** was obtained as yellowish to orange solid with a yield of 40 % (0.156 g). This yield is lower than what is reported in literature for similar compounds, probably due to the use of different leaving group on the **SP2** (chloro rather than iodo).

- ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.32 (s, 1H), 8.18 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.93 (d, *J* = 17.1 Hz, 2H), 7.03 (d, *J* = 10.4 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 1H), 5.85 (d, 9 Hz, 1H), 3.56 (m, 2H), 3.15 – 1.90 (m, 32H), 1.38 (s, 21H), 1.26 (s, 3H), 1.18 (s, 3H).
- ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 173.7, 173.3, 172.6, 157.2, 152.4, 140.9, 140.8, 136.4, 129.5, 128.2, 126.4, 123.6, 122.4, 120.0, 118.5, 118.0, 106.6, 105.9, 83.0, 82.4, 56.9, 55.7, 51.9, 50.4, 46.7, 43.6, 33.6, 29.1, 27.8, 27.7, 25.8, 19.8.

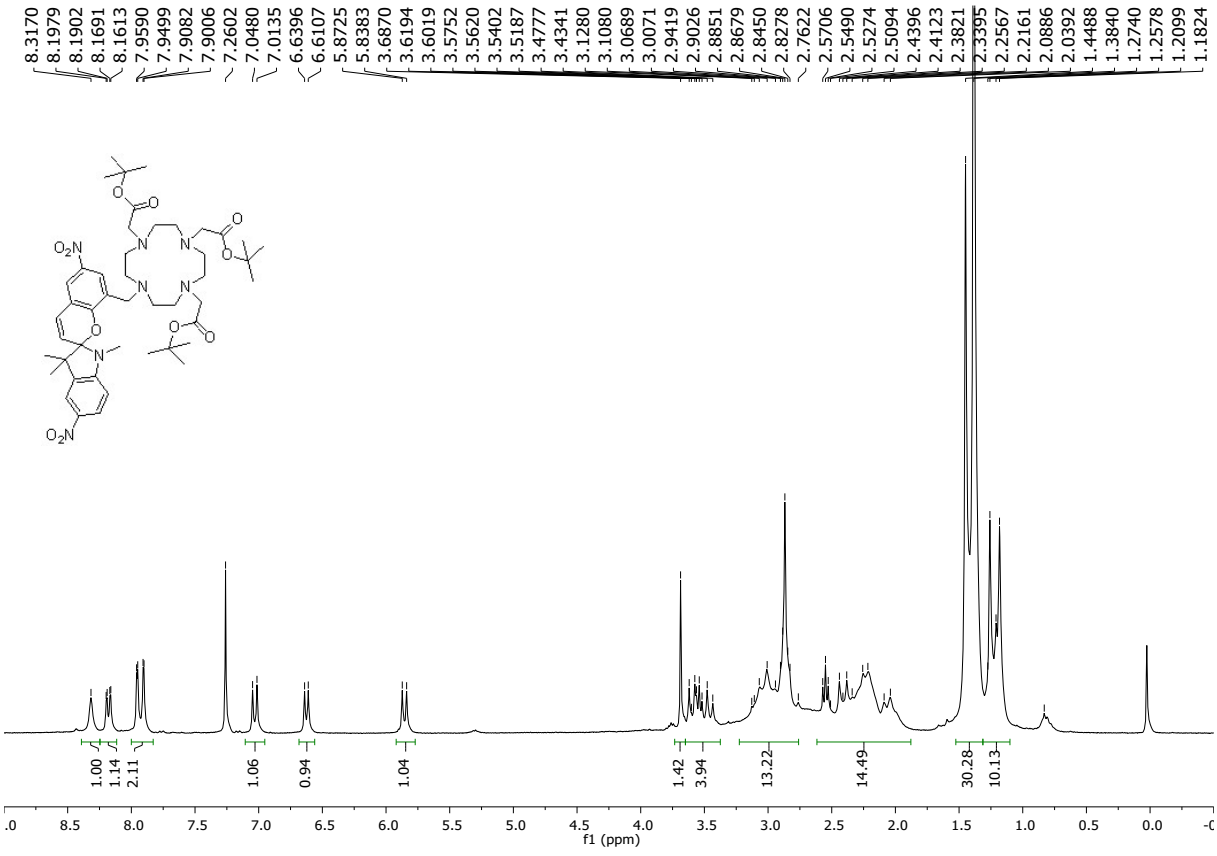


*Figure S13 : ^{1}H NMR of compound **2** ($CDCl_3$, 300 MHz, 298K).*

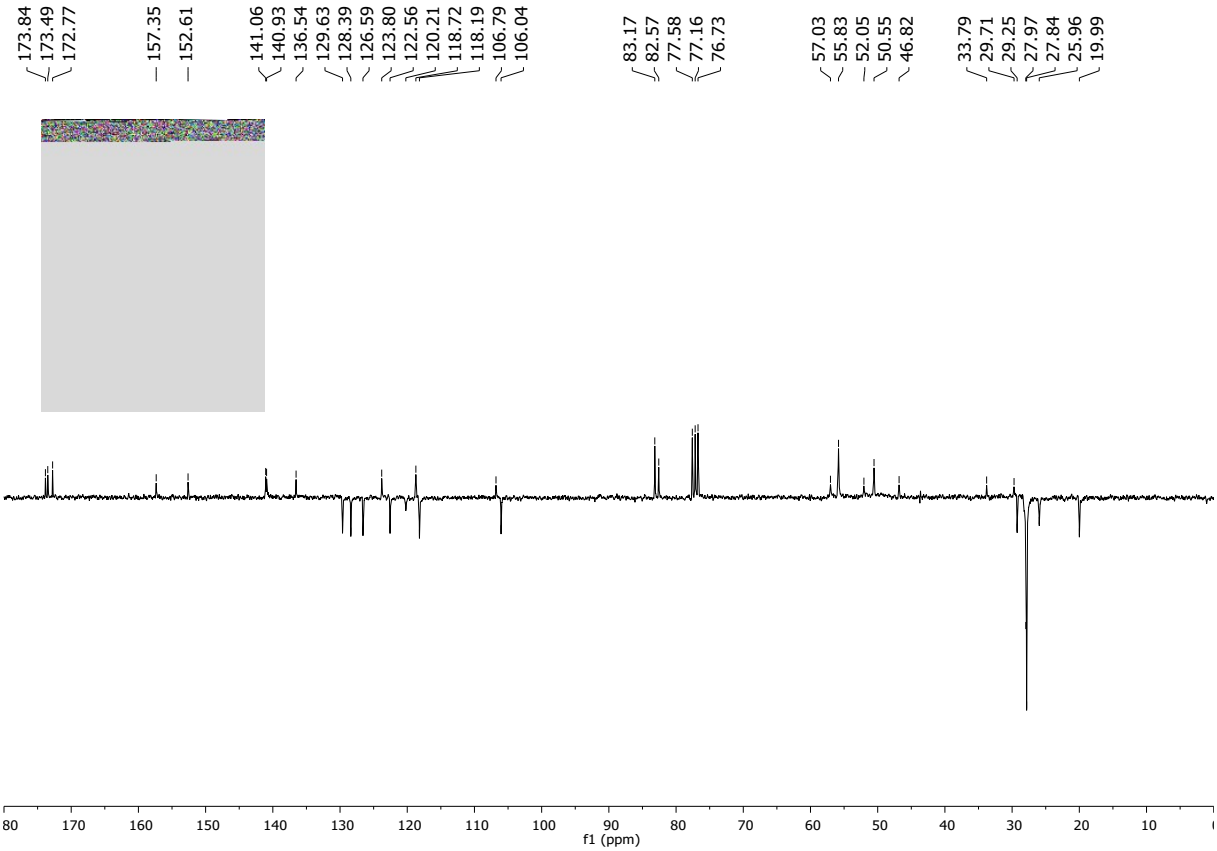
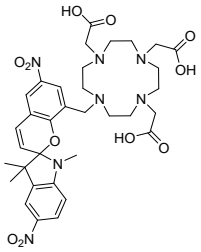


*Figure S14 : ^{13}C NMR of compound **2** ($CDCl_3$, 126 MHz, 298K).*



Synthesis of L2: Compound **L2** was synthesized as described in literature. [3] The compound was never isolated pure due to the presence of residual TFA salts. It was used directly for the next step, and this did not affect the complexation step. The compound was obtained as dark pink solid.

- ^1H NMR (400 MHz, CD_3OD): δ (ppm) = 8.45 (d, *J* = 2.4 Hz, 1H), 8.30 (dd, *J* = 4,8 Hz, 2H), 8.06 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 10.5 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.13 (d, *J* = 10.4 Hz, 1H), 3.02 (s, 3H), 1.31 (s, 3H), 1.24 (s, 3H).
- ^{13}C NMR (126 MHz, CD_3OD): δ (ppm) = 157.6, 151.9, 141.1, 140.6, 136.2, 129.0, 128.7, 125.7, 124.0, 120.5, 119.8, 117.7, 108.2, 108.2, 105.3, 51.9, 50.9, 49.6, 28.8, 27.4, 23.9, 17.9.

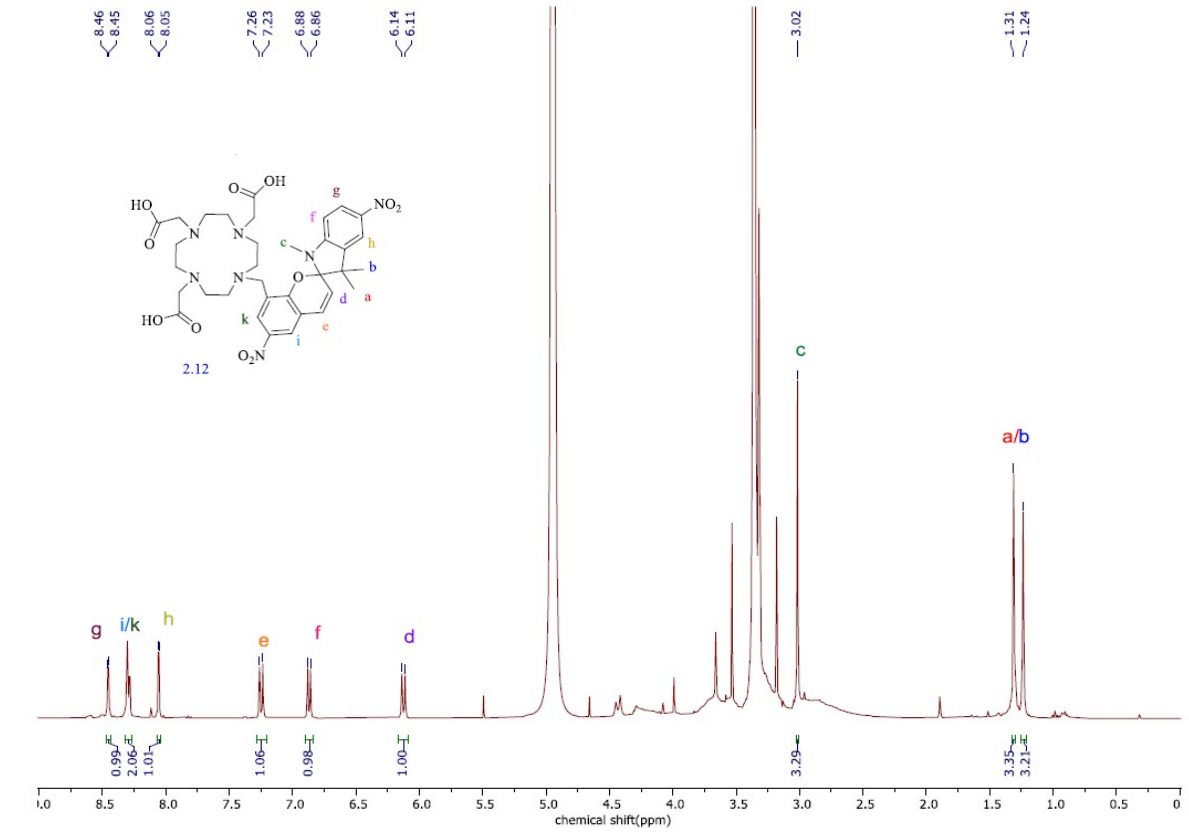


*Figure S15 : [1]H NMR of compound **L2** (CD_3OD, 400 MHz, 298K).*

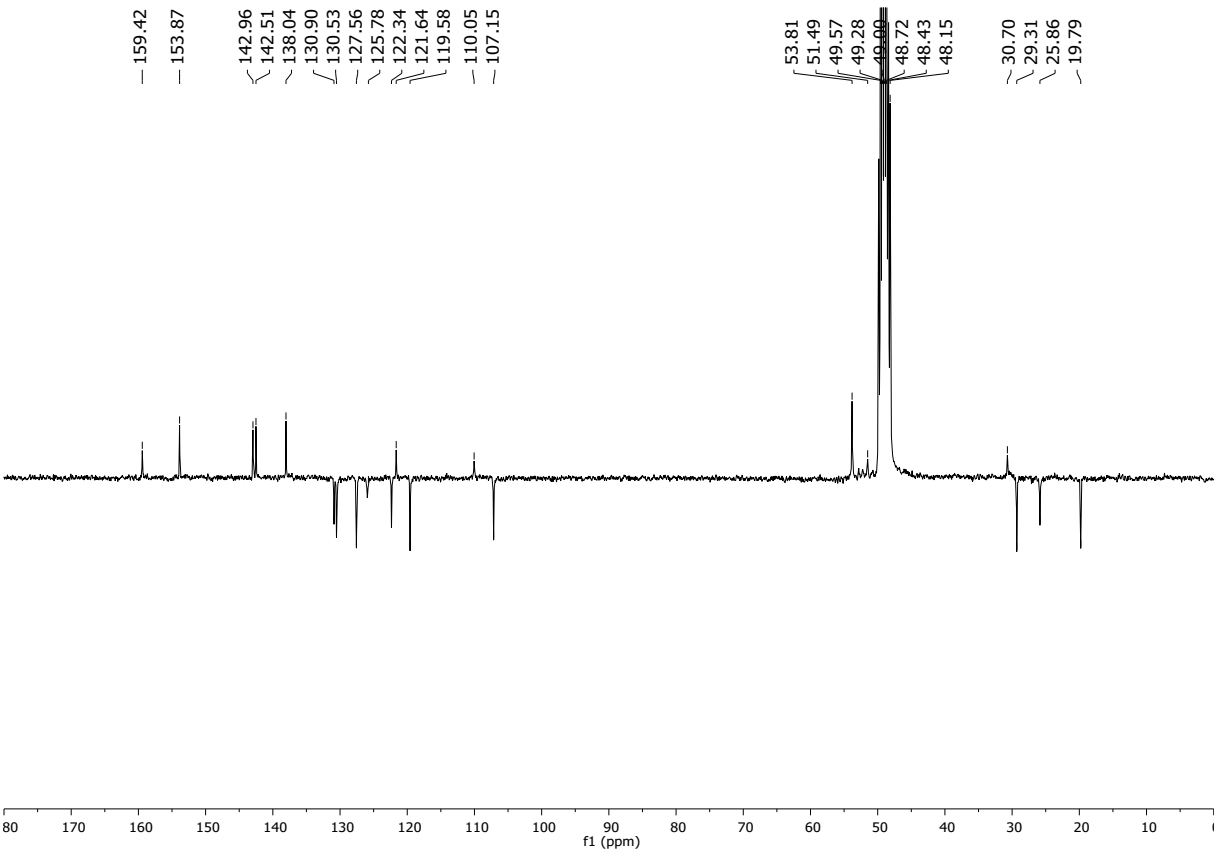
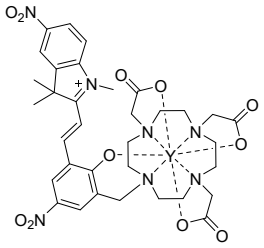


*Figure S16 : [13]C NMR of compound **L2** (CD_3OD, 126 MHz, 298K).*



Synthesis of compound 2Y: Into a solution of **L2** (0.202 g, 0.278 mmol, 1 eq) in 20 mL of methanol was added $YCl_3.6H_2O$ (0.085 g, 0.278 mmol, 1eq). The reaction mixture was refluxed overnight before evaporation of solvents to dryness. The crude product was purified by silica column chromatography using CH_2Cl_2: CH_3OH: H_2O (1:4:1) as eluent to give compound **2Y** (0.149 g, % yield = 66 %) as a red solid.

- ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) = 8.6-8.7 (m, 3H), 8.49 (dd, *J* = 8.8, 2.2 Hz, 1H), 8.38 (d, *J* = 16.0 Hz, 1H), 8.20 (d, *J* = 3.1 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 4.7-2.1 (m, 24H), 4.28 (s, 3H), 1.90 (bs, 6H).
- ESI-HR-MS (positive, MeOH): *m/z* calcd. for $[C_{34}H_{41}N_7O_{11}Y]^+$: 812.19171, found: 812.1918.
- FT-IR (cm^{-1}, ATR): 1593 (C=O), 1514, 1310 (C=C), 1241, 1205, 1107, 1081, 968, 934, 903.

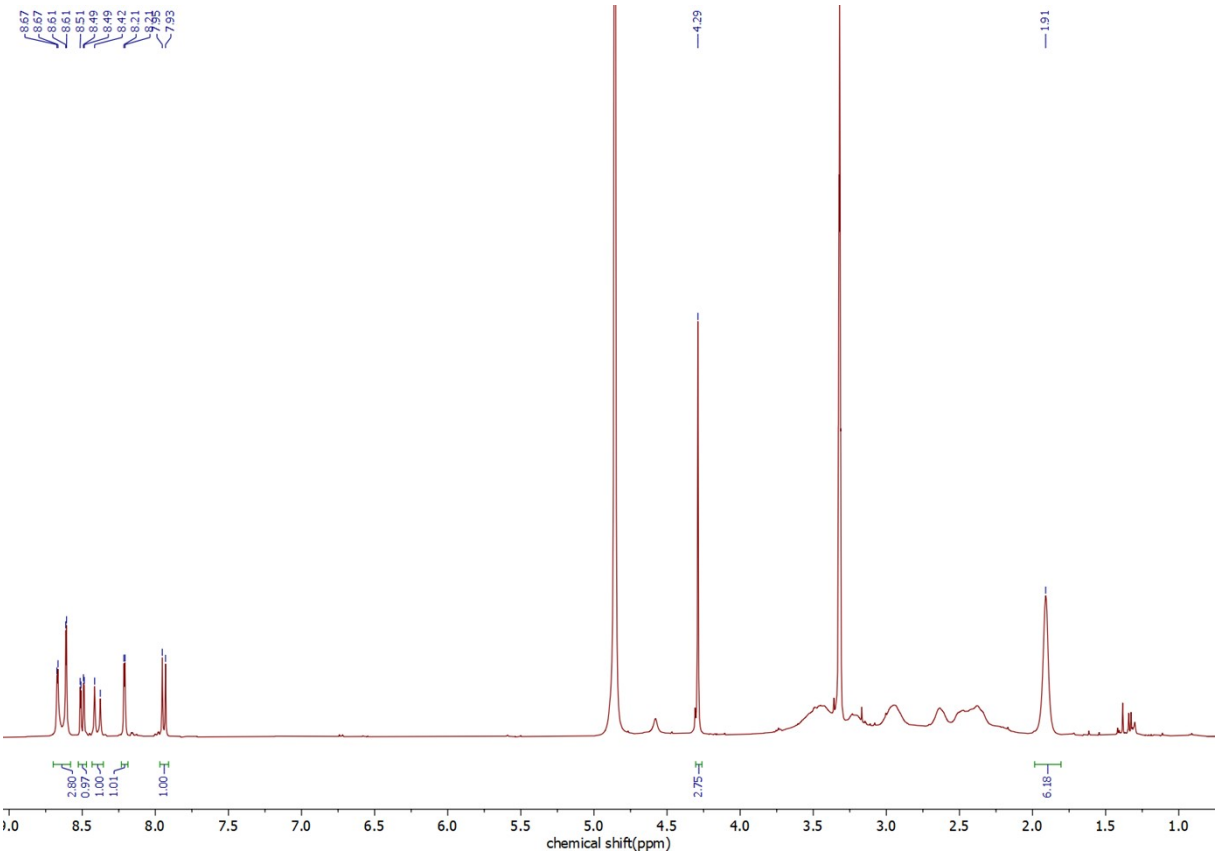
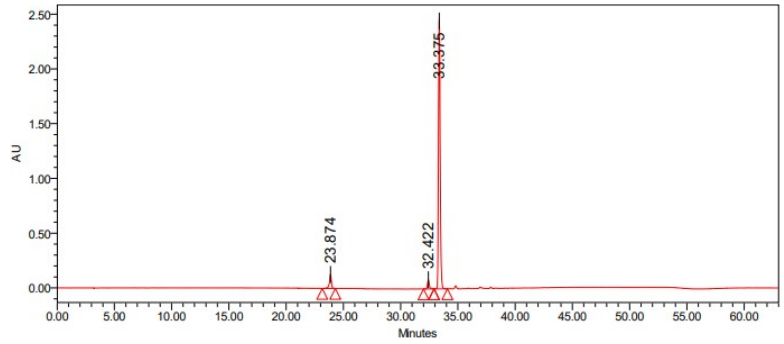


*Figure S17: ^{3}H NMR of compound **2Y** (400 MHz, CD_3OD, 298K).*



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 360.0 nm	23.874	1532471	5.52	128463
2	PDA 360.0 nm	32.422	924438	3.33	84365
3	PDA 360.0 nm	33.375	25308477	91.15	2452719

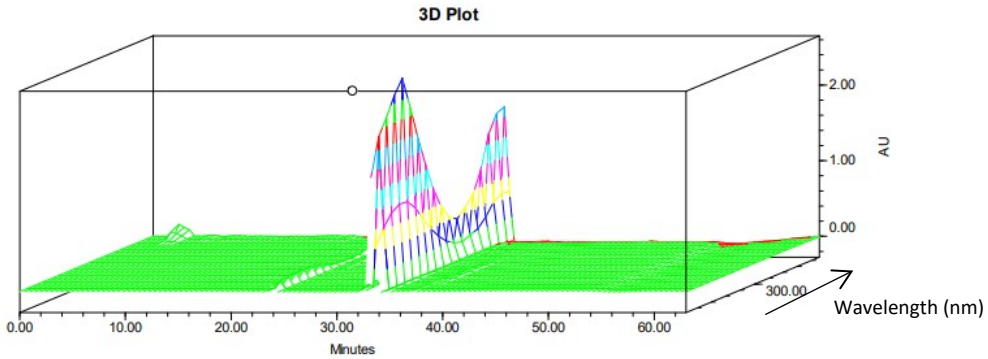
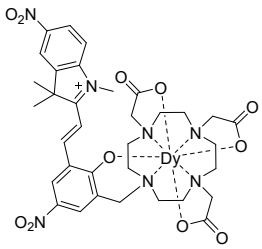
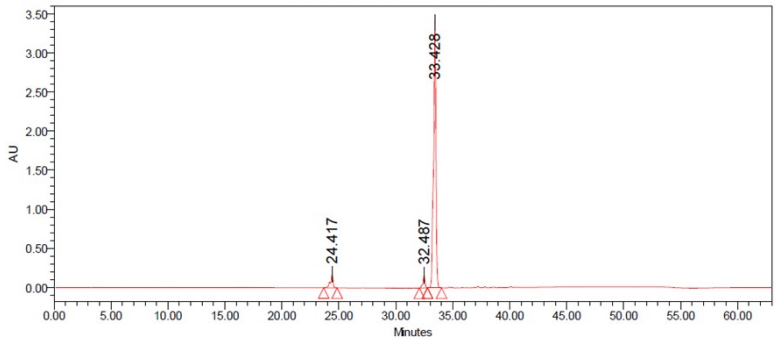


*Figure S18: HPLC-UV-DAD analysis of compound **2Y**. Column: MODULO-CART QK UPTISPHERE 5 ODB 250 x 4.6 mmUP50DB-25QK. Gradient: 5% MeOH – 95 % H_2O. Injection volume 20.00 ul. λ = 360 nm. Retention time = 33.375 min, purity = 91 %.*



Synthesis of 2Dy: Into a solution of **L2** (0.17g, 0.234 mmol, 1eq), in 20 mL of methanol was added $DyCl_3.6H_2O$ (0.088g, 0.234mmol, 1eq). The reaction mixture was refluxed overnight before the evaporation of solvents to dryness. The crude product was purified by silica column chromatography using CH_2Cl_2: CH_3OH: H_2O (1:4:1) as eluent to afford compound **2Dy** (0.141 g, % yield = 68 %) as a red solid.

- ESI-HR-MS (positive, MeOH): *m/z* calcd. for $[C_{34}H_{43}DyN_6O_9]^+$: 421.6186 , found: 421.6192 , $[M+2H]^{2}+$; calcd. for $[C_{34}H_{41}DyN_7O_{11}]^+$: 887.21559 , found: 887.2159, $[M+H]^+$
- FT-IR (cm^{-1}, ATR): 1593 (C=O), 1514, 1311, 1242, 1204, 1111, 1084, 970, 935, 903.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 360.0 nm	24.417	2701944	5.10	172508
2	PDA 360.0 nm	32.487	2017948	3.81	162078
3	PDA 360.0 nm	33.428	48311001	91.10	3330572

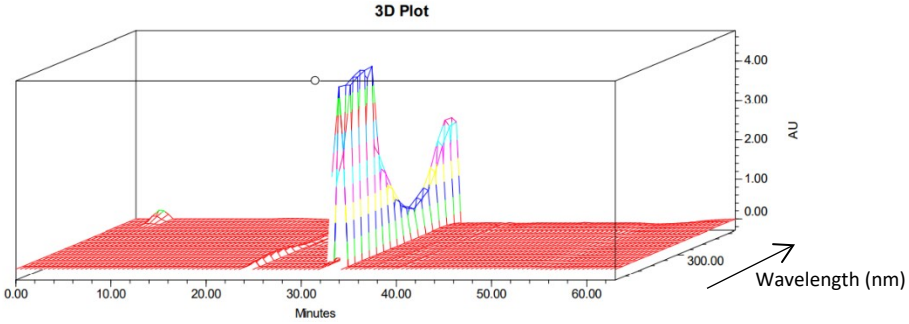


Figure S19: HPLC-UV-DAD analysis of compound ***2Dy****. Column: MODULO-CART QK UPTISPHERE 5 ODB 250 x 4.6 mmUP50DB-25QK. Gradient: 5% MeOH – 95 % H_2O. Injection volume 20.00 ul. λ = 360 nm. Retention time = 33.428 min, purity = 91 %.*

X-Ray Diffraction Analysis

For 1Y: ($C_{34}H_{41}N_6O_9Y$, C_2H_3N); M = 807.69 g.mol^{-1}. A suitable crystal for X-ray diffraction single crystal experiment (orange prism, dimensions = 0.07 x 0.090 x 0.160 mm) was selected and mounted on the goniometer head of a D8 Venture AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, [*], Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), *T* = 150(2) K; Crystal structure has been described in monoclinic *P* $2_1/c$ (I.T.#14) space group. Cell parameters were refined as shown in Table S1. The structure was solved by dual-space algorithm using the *SHELXT* program,[4] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[5] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 8275 unique intensities and 482 parameters converged at $\omega R(F^2)$ = 0.0927 ($R(F)$ = 0.0419) for 7562 observed reflections with $I > 2\sigma(I)$.

For 2Y: ($C_{34}H_{40}N_7O_{11}Y$); *M* = 811.64 g.mol^{-1}. A suitable crystal for X-ray diffraction single crystal experiment (orange plate, dimensions = 0.330 x 0.250 x 0.060 mm) was selected and mounted on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector [*], using Mo-*Kα* radiation (*λ* = 0.71073 Å, graphite monochromator) at *T* = 150(2) K. Crystal structure has been described in triclinic symmetry and *P* -1 (I.T.#2) centric space group. Cell parameters have been refined as shown in Table S2. Number of formula unit *Z* is equal to 2 and calculated density *d* and absorption coefficient μ values are 1.214 g.cm^{-3} and 1.370 mm^{-1} respectively. Crystal structure was solved by dual-space algorithm using *SHELXT* program,[4] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[5] The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,[6] implemented as the *SQUEEZE* option in *PLATON*.[7] A new data set, free of solvent contribution, was then used in the final refinement. All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 10132 unique intensities and 481 parameters converged at ωR_F^2 = 0.1190 (R_F = 0.0477) for 8709 observed reflections with $I > 2\sigma(I)$.

For 2Dy-H_2O: ($C_{34}H_{42}DyN_7O_{12}$[+solvent]); *M* = 903.24. A suitable crystal for X-ray diffraction single crystal experiment (red plate, dimensions = 0.080 x 0.130 x 0.390 mm) was selected and mounted on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo-*Kα* radiation (*λ* = 0.71073 Å, multilayer monochromator) at *T* = 150(2) K. Crystal structure has been described in monoclinic symmetry and *C* 2/*c* (I.T.#15) centric space group (R_{int} = 0.0557). Cell parameters have been refined as follows: *a* = 52.331(6), *b* = 11.4130(13), *c* = 16.8157(19) Å, *β* = 105.896(5) °, *V* = 9659.2(19) Å^3. Number of formula unit *Z* is equal to 8 and calculated density *d* and absorption coefficient μ values are 1.242 g.cm^{-3} and 1.602 mm^{-1} respectively. Crystal structure was solved by dual-space algorithm using *SHELXT* program, [4] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[5] The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm ,[6] implemented as the *SQUEEZE* option in *PLATON*.[7] A new data set, free of solvent contribution, was then used in the final refinement. All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. Except H12A and H12B that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 11047 unique intensities and 496 parameters converged at ωR_F^2 = 0.0824 (R_F = 0.0320) for 8764 observed reflections with $I > 2\sigma(I)$.

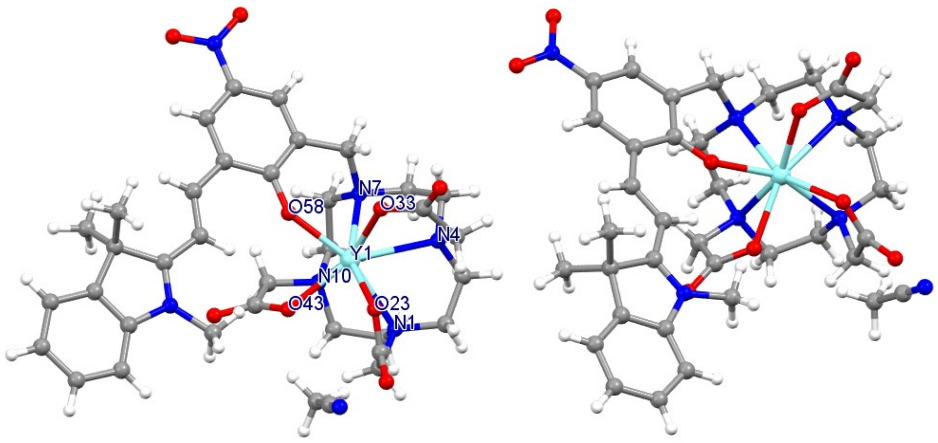


*Figure S20: View of the structure of compound **1Y** obtained by SC-XRD showing the MC state of the photochromic unit (left) and the 8 coordinated Y(III) center (right).*

*Table S1: Crystallographic data collected for compound **1Y**.*

	Compound **1Y** **[Y(L1)](CH$_3$CN)**
T (K)	150
Symmetry, space group	Monoclinic, *P 2$_1$/c*
a, b, c (Å)	12.4815 (12), 7.6027(6), 38.132(3)
β (°)	95.013(3)
Volume (Å^3)	3604.6(5)
Z	4
Calculated density (g.cm^{-3})	1.488

*Table S2: Bond length in the coordination sphere of the metal center of compound **1Y**.*

	Bond length (Å)
Y1 – O58	2.2552(17)
Y1 – O23	2.2667(18)
Y1 – O43	2.2959(17)
Y1 – O33	2.3127(18)
Y1 – N1	2.571(2)
Y1 – N7	2.576(2)
Y1 – N10	2.591(2)
Y1 – N4	2.622(2)

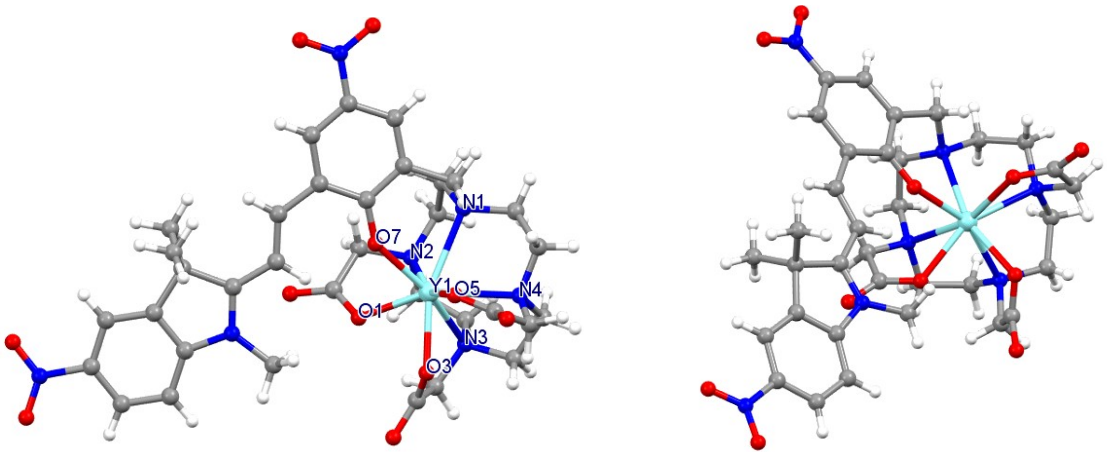


*Figure S21: View of the structure of compound **2Y** obtained by SC-XRD showing the MC state of the photochromic unit (left) and the 8 coordinated Y(III) center (right).*

*Table S3: Crystallographic data collected for compound **2Y**.*

	Compound **2Y** (Squeezed) **[Y(L2)]**
T (K)	150
Symmetry, Space group	Triclinic, *P -1*
a, b, c (Å)	9.4468(10), 15.103(2), 16.446(2)
α, β, γ (°)	84.413(4), 76.829(4), 76.662(4)
Volume (Å^3)	2220.6(5)
Z	2
Calculated density (g.cm^{-3})	1.214

*Table S4: Bond lengths in the coordination sphere of the metal center of compound **2Y**.*

	Bond length (Å)
Y1 - O7	2.2477(18)
Y1 – O5	2.292(2)
Y1 – O1	2.2982(19)
Y1 – O3	2.312(2)
Y1 – N1	2.563(2)
Y1 – N4	2.565(2)
Y1 – N2	2.578(2)
Y1 – N3	2.578(3)

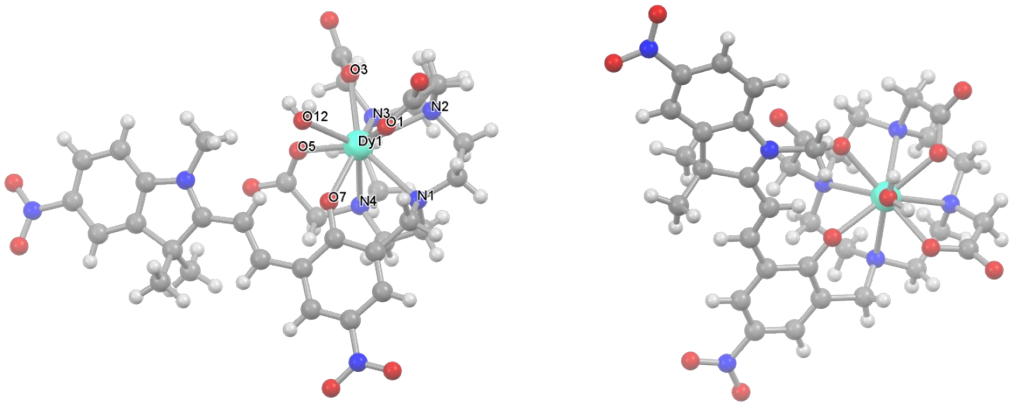


*Figure S22: View of the structure of compound **2Dy-H_2O** obtained by SC-XRD showing the MC state of the photochromic unit (left) and the 9 coordinated Dy(III) center (right).*

*Table S4: Crystallographic data collected for compound **2Dy-H_2O**.*

	Compound **2Dy-H_2O** (Squeezed) **[Dy(L2)(H_2O)]**
T (K)	150
Symmetry, Space group	Monoclinique, *C2/c*
a, b, c (Å)	52.331(6) 11.4130(13) 16.8157(19)
β (°)	105.896(5)
Volume (Å^3)	9659.2(19)
Z	8
Calculated density (g.cm^{-3})	1.242

*Table S5: Bond lengths in the coordination sphere of the metal center of compound **2Dy-H_2O**.*

	Bond length (Å)
Dy1 - O7	2.3252(19)
Dy1 – O5	2.309(2)
Dy1 – O1	2.315(2)
Dy1 – O3	2.344(2)
Dy1 – N1	2.661(2)
Dy1 – N4	2.653(3)
Dy1 – N2	2.638(3)
Dy1 – N3	2.663(3)
Dy1- O12	2.477(2)

Optical properties

In all cases, the samples were kept in the dark until no evolution of their spectrum occurs. Irradiations were performed with a Xenon lamp through a 450 nm or 530 nm bandpass filter (10 nm HBW) from Thorlabs company. One of these wavelengths was selected in order to match the low energy absorption band of the studied compound. The measured power of irradiation at the sample position was 3 mW for 450 nm and 1.7 mW for 530 nm. Given that the beam size is approximately 6 cm^2 , the irradiance was 0.5 $mW.cm^{-2}$ at 450 nm and 0.3 $mW.cm^{-2}$ at 530 nm. The same set up was used for KBr samples.

Alternatively, for **1Y** and **2Dy**, time-profiles were obtained on a homemade photokinetic setup, by monitoring the change of the absorption spectrum overtime, while the sample is continuously irradiated at 450 nm or at 530 nm, under continuous stirring (400 rpm) at T = 20°C. The temperature and stirring were controlled thanks to a Peltier device. The irradiation wavelength (source Xe lamp Zolix instruments, model Sitius 300P) was selected by passing through a monochromator (Zolix instruments, model Omni-λ200i, halfwidth of ± 10 nm). Absorption spectra were acquired with a Flame spectrophotometer (Ocean Insights) combined to a DHBAL-2000 D/Hal lamp. Light intensity was measured using a Thorlabs (PM100USB) powermeter. Experimental data are a matrix of full spectra over the full time of acquisition; useful photokinetic profiles were extracted at the maximum of absorbance of the corresponding isomer (Figures S23-S26). For the isomerization reaction investigated here, consisting of two states (equilibrium starting state **i** and after irradiation state **f**) where the equilibrium starting state to photostationnary state thermal back reaction is neglected, the time evolution of the mixture composition under light irradiation is described by the general differential equation (Eq. S1):

$$\frac{dC_i(t)}{dt} = -\frac{dC_f(t)}{dt} = \phi_{i\to f} I_i^{abs}(\lambda_{irr},t) - \phi_{f\to i} I_f^{abs}(\lambda_{irr},t) \qquad \text{(Eq. S1)}$$

where t is time, $C_i(t)$ and $C_f(t)$ are the concentrations of equilibrium starting state **i** and after irradiation state **f**, respectively; $\phi_{i\to f}$ and $\phi_{f\to i}$ are the forward and return reactions quantum yields,

respectively; and $I_i^{abs}(\lambda_{irr},t)$ and $I_f^{abs}(\lambda_{irr},t)$ are the intensities of the irradiated light absorbed by equilibrium starting state and after irradiation state.

In the general case, (Eq. S1) has no analytical solution because $I_i^{abs}(\lambda_{irr},t)$ and $I_f^{abs}(\lambda_{irr},t)$ vary by several means over time. At $t = 0$, however, the solution contains only equilibrium starting state, and the initial parameters required to determine these intensities are known. It is also possible to neglect the back reaction since no isomerized species is present in solution yet. Under these conditions, the quantum yield $\phi_{i\to PSS}$ can be determined from (Eq. S2):

$$\phi_{i\to f} = \frac{1}{\epsilon_f(\lambda_{obs}) I_0 \left(1 - 10^{\epsilon_i(\lambda_{irr}) l C_{tot}}\right) I} \left(\frac{dA_f}{dt}\right)_{t=0} \qquad \text{(Eq. S2)}$$

where I_0 is the initial incident photon flux $mol.photon.s^{-1}.L^{-1}$, ϵ_i is the molar extinction coefficients of equilibrium starting state **i** and ϵ_f after irradiation state, respectively, and $(dA_f/dt)_{t=0}$ is the initial slope of the absorbance–time curve for the isomerized form. (Eq. S2) is applied by fitting the measured absorbance curve to an exponential function and computing its derivative at $t = 0$ to extract $\phi_{i\to f}$.

The thermal cycloreversion reactions were monitored by recording absorption spectra at T = 20°C every 30 s with a Flame spectrophotometer (Ocean Insights) combined to a DHBAL-2000 D/Hal lamp equipped with an internal synchronized shutter.

The time-profiles were fitted with an exponential function of the kind (Eq. S3):

$$A = A_0 + A_1 e^{-kt} \qquad \text{(Eq. S3)}$$

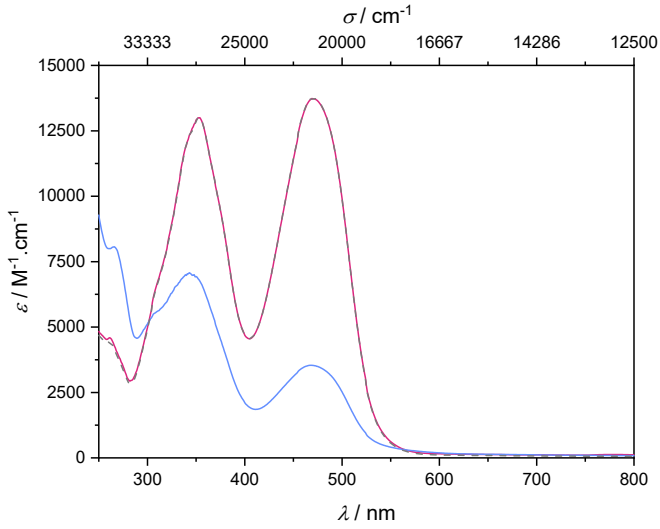


*Figure S23 : Electronic absorption spectra of complex **1Y** in methanol at equilibrium state (magenta line), after irradiation (blue line) and upon resting in the dark (dotted gray line). Irradiation was performed at 450 nm (0.6 mW.cm^{-2}). Irradiation and resting times are as follow: 450 nm – 10 min, dark – 5 h. T = 20°C, C = 3.10^{-5}M.*

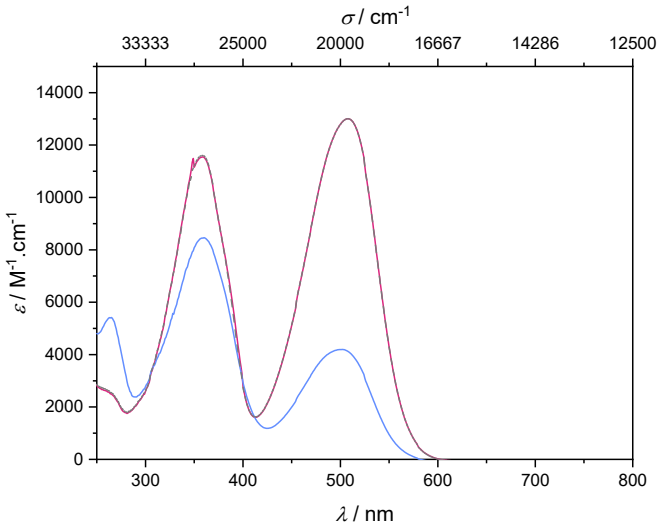


*Figure S24 : Electronic absorption spectra of complex **2Dy** in methanol at equilibrium state (magenta line), after irradiation (blue line) and upon resting in the dark (dotted gray line). Irradiation was performed at 450 nm (0.35 mW.cm^{-2}). Irradiation and resting times are as follow: 530 nm – 30 min, dark – 12 h. T = 20°C, C = 2.10^{-5}M.*

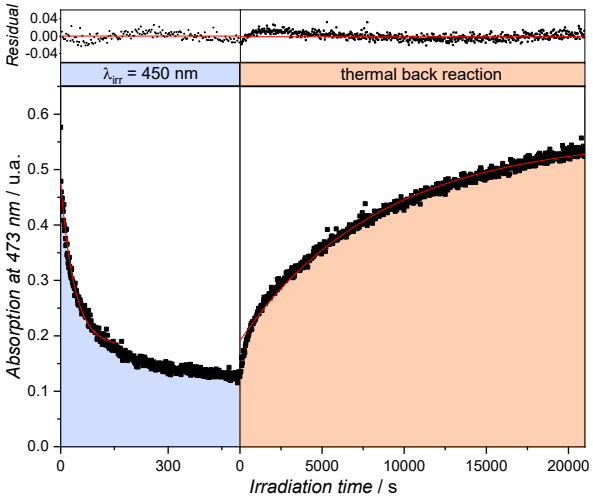


*Figure S25 : Continuous absorption time–evolution profile extracted at 473 nm for **1Y** during a full cycle of photoisomerization under continuous 450 nm illumination and thermal back reaction. From this data we extract an isomerization quantum yield* $\phi_{i\to f} =$ *0.6 ± 0.1 and a thermal return constant k = 4.7 10^{-5} s^{-1}.*

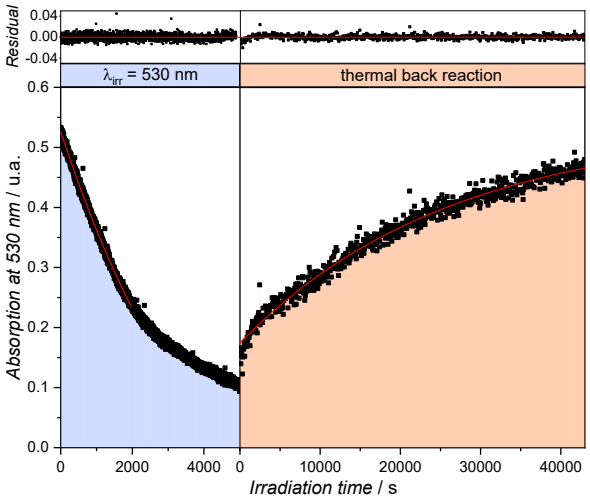


Figure S26 : Continuous absorption time–evolution profile extracted at 530 nm for ***2Dy*** *during a full cycle of photoisomerization under continuous 530 nm illumination and thermal back reaction. From this data we extract an an isomerization quantum yield* $\phi_{i \to f} =$ *0.5 ± 0.1 and a thermal return constant k = 5.0* 10^{-6} s^{-1}.

1- **Compound 2Y:**

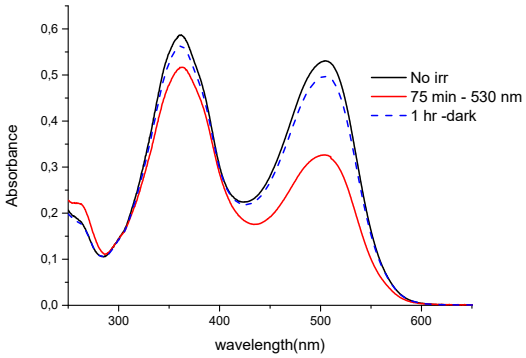


Figure S27: Absorption spectra of compound ***2Y*** *in methanol: (black) six hours in the dark; (red) irradiated with visible light λ = 530 nm for 75 min; (navy blue) then kept in the dark 1 hour.*

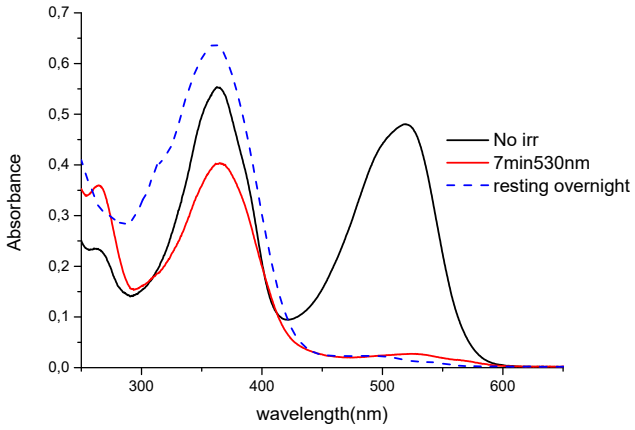


Figure S28: Absorption spectra of compound ***2Y*** *in dichloromethane: (black) six hours in the dark; (red) irradiated with visible light 530 nm) for 7 min; (navy blue) then kept in the dark overnight.*

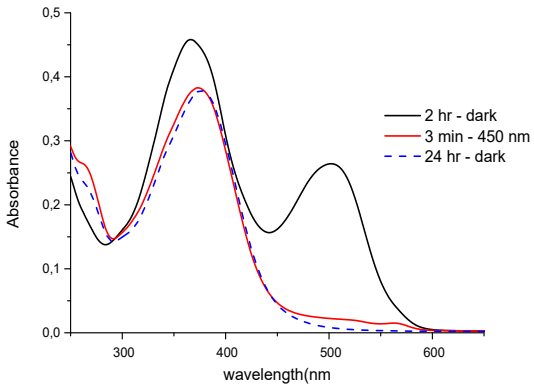


*Figure S29: Absorption spectra of compound **2Y** in acetonitrile: (black) two hours in the dark; (red) irradiated with visible light (450 nm) for 3 min; (navy blue) then kept in the dark for 24 hours.*

2- **Compound 2Dy:**

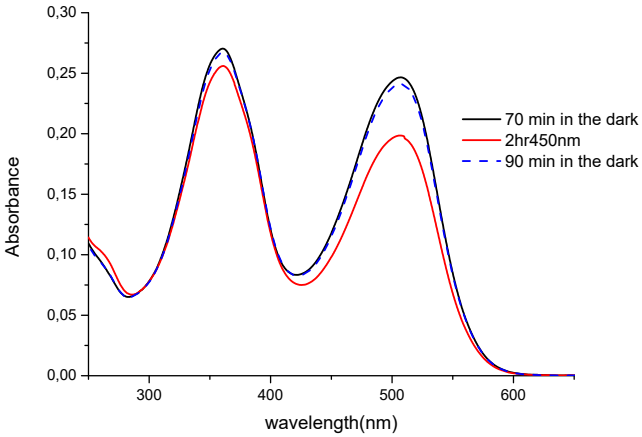


*Figure S30: Absorption spectra of compound **2Dy** in methanol before irradiation/PSS (black), after light irradiation at 450 nm for 2 hours (red), and after standing in the dark for 90 minutes (navy blue).*

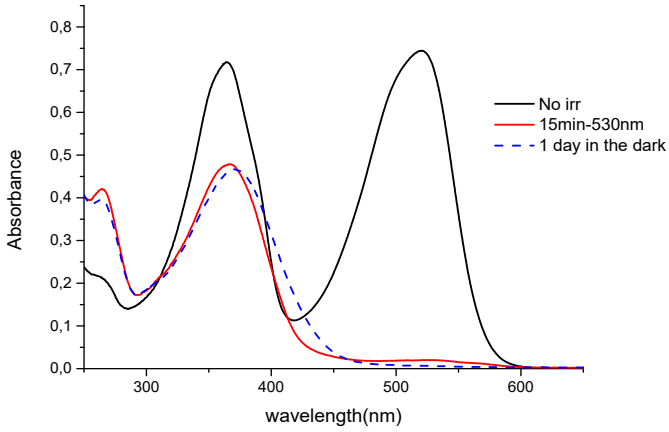


Figure S31: Absorption spectra of compound 2Dy in dichloromethane before irradiation/PSS (black), after visible light irradiation for 15 minutes (red), and after standing in the dark for 24 hours (navy blue).

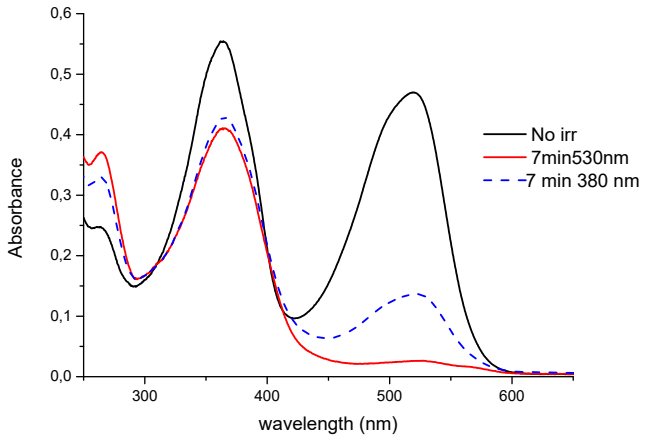


*Figure S32: Absorption spectra of compound **2Dy** in dichloromethane before irradiation/PSS (black), after visible light irradiation for 7 minutes (red), and after UV light irradiation for 7 minutes (navy blue).*

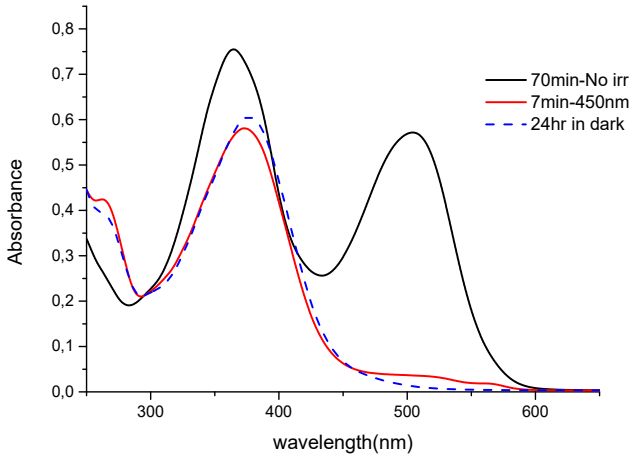


*Figure S33 : Absorption spectra of compound **2Dy** in acetonitrile before irradiation/PSS (black), after visible light irradiation for 7 minutes (red), and after standing in the dark for 24 hours (navy blue).*

3- **Compound 1Y:**

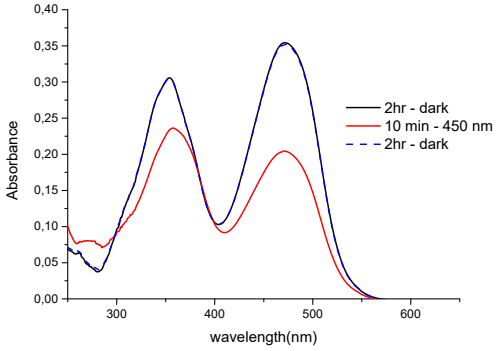


*Figure S34: Absorption spectra of compound **1Y** in methanol: (black) two hours in the dark; (red) irradiated with visible light λ = 450 nm for 10 min; (navy blue) then kept in the dark for 2 hours.*

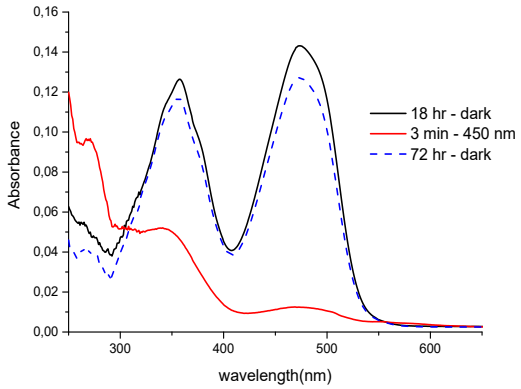


*Figure S35: Absorption spectra of compound **1Y** in dichloromethane: (black) overnight in the dark; (red) irradiated with visible light λ = 450 nm for 3 min; (navy blue) then kept in the dark for 3 days.*

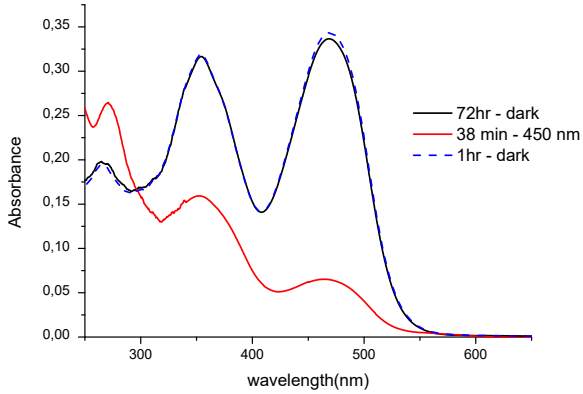


*Figure S36: Absorption spectra of compound **1Y** in acetonitrile: (black) three days in the dark; (red) irradiated with visible light λ = 450 nm for 38 min; (navy blue) then kept in the dark for 1 hour.*

4- **Compound 1Dy:**

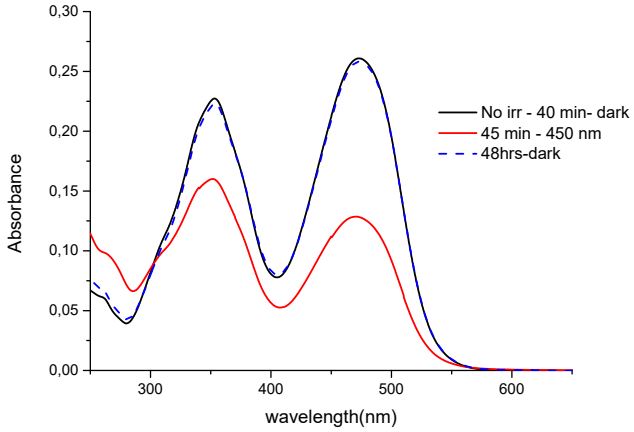


*Figure S37: Absorption spectra of compound **1Dy** in methanol before irradiation/PSS (black), after light irradiation at 450 nm for 45 minutes (red), and after successively standing in the dark for 48 hours (navy blue).*

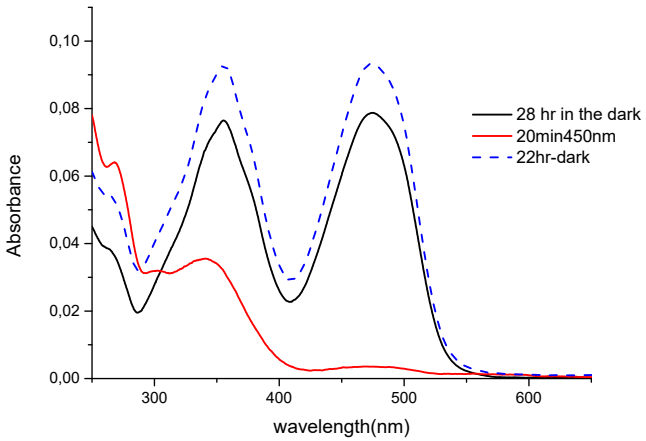


*Figure S38: Absorption spectra of compound **1Dy** in dichloromethane before irradiation/PSS (black), after light irradiation at 450 nm for 20 minutes (red), and after standing in the dark for 22 hours (navy blue).*

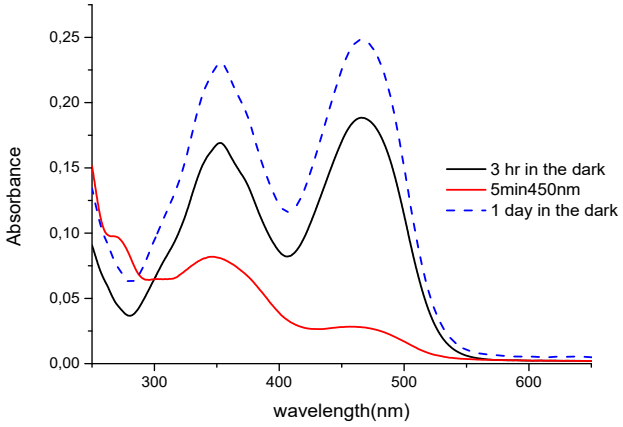


*Figure S39: Absorption spectra of compound **1Dy** in acetonitrile before irradiation (black), after visible light irradiation for 5 minutes (red), and after standing in the dark for 24 hours (navy blue).*

- Following of the photoisomerization of compound **1Y** by ^{1}H NMR:

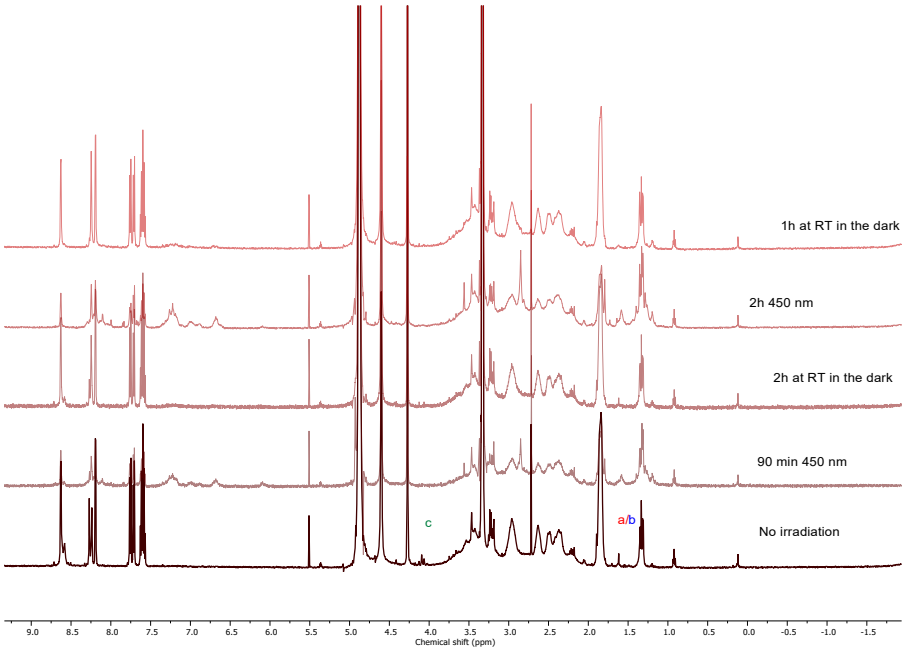


*Figure S40: ^{1}H NMR (CD_3OD, 400 MHz) of **1Y** without irradiation, after visible light irradiation at λ = 450 nm for 90 minutes, after storing the solution in the dark for two hours at room temperature, after two hours of light irradiation (λ = 450 nm), and finally storing the solution in the dark for one hour at room temperature. Note that one alkene proton observed as a doublet at 8.61 ppm gradually disappears during the experiment, due to deuteration,[8] and as a consequent the second alkene proton seen at 8.24 ppm gradually turns into a singlet.*

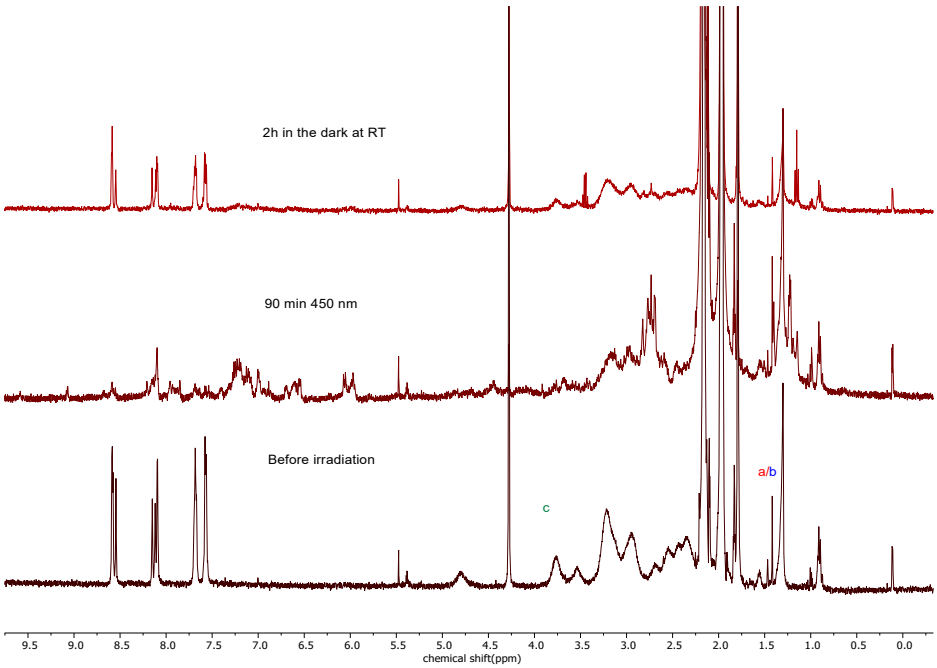


*Figure S41: ^{1}H NMR (CD_3CN, 400 MHz) of **1Y** without irradiation, after visible light irradiation at λ = 450 nm for 90 minutes, and after storing the solution in the dark for two hours at room temperature.*

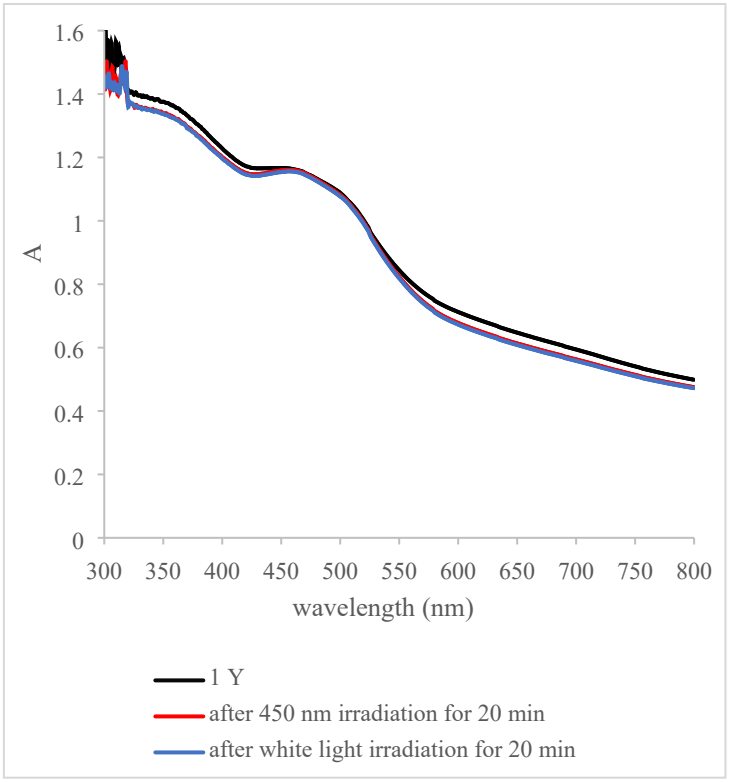


*Figure S42: Absorption spectrum of **1Y** in a KBr pellet before (black line) and after 450 nm (3 mW.cm^{-2}) irradiation for 20 min (red line). Further irradiation with white light did not modify the spectrum (blue line).*

Theoretical Calculations

Computational details

Wavefunction-based calculations were carried out on the optimized molecular structures (*vide infra*) of the merocyanine (left) and spiropyran (right) forms of **1Dy** complexes by using the SA-CASSCF/RASSI-SO approach, as implemented in the OpenMolcas quantum chemistry package (versions 22.10).[8] In this approach, the relativistic effects are treated in two steps on the basis of the Douglas–Kroll Hamiltonian. First, the scalar terms were included in the basis-set generation and were used to determine the spin-free wavefunctions and energies in the complete active space self-consistent field (CASSCF) method.[9] Next, spin-orbit coupling was added within the restricted-active-space-state-interaction (RASSI-SO) method, which uses the spin-free wavefunctions as basis states.[10] Spin−orbit (SO) integrals are calculated using the AMFI (atomic mean- field integrals) approximation.[11] The resulting wavefunctions and energies are used to compute the magnetic properties and g-tensors of the lowest states from the energy spectrum by using the pseudo-spin S = 1/2 formalism in the SINGLE-ANISO routine.[12] Cholesky decomposition of the bielectronic integrals was employed to save disk space and speed-up the calculations.[13] The active space consisted of the nine 4f electrons of the Dy^{III} ion spanning the seven 4f orbitals, i.e. CAS(9,7)SCF. State-averaged CASSCF calculations were performed for all of the sextets (21 roots), all of the quadruplets (224 roots), and 300 out of the 490 doublets of the Dy^{III} ion. 21 sextets, 128 quadruplets, and 107 doublets were mixed through spin−orbit coupling in RASSI-SO. All atoms were described by ANO-RCC basis sets.[14] The following contractions were used: [8s7p4d3f2g1h] for Dy, [4s3p2d] for O and N, [3s2p1d] for C and [2s] for H. Geometries were optimized with the AMS program suite (revision 2019.302).[15] These calculations utilized the scalar all-electron zeroth-order regular approximation (ZORA)[16] along with the revPBE (Perdew-Burke-Ernzerhof) functional.[17] For all atoms, the atomic basis set corresponded to the triple-ζ polarized (TZP) Slater-type orbital (STO) all-electron basis set.[18] Solvent (dichloromethane, methanol) was taken into account through Conductor like Screening Model (COSMO) of solvation.[19]

*Table S6: Calculated relative energies (in kcal.mol^{-1}) between MC and SP forms for **1M** and **2M** (M = Y, Dy) complexes.*

	Gas phase		Dichloromethane		Methanol	
	MC	SP	MC	SP	MC	SP
1Y	0.0	20.4	0.0	25.1	0.0	25.2
1Dy	0.0	22.2	0.0	25.4	0.0	25.2
2Y	0.0	17.0	0.0	18.1	0.0	17.9
2Dy	0.0	17.0	0.0	18.0	0.0	19.2

*Table S7: Computed energies levels (the ground state is set at zero), component values of the Lande factor g and wavefunction composition for each M_J state of the ground-state multiplet for the Dy center in the merocyanine form of **1-Dy** (gas phase optimized structure). Calculations carried out at the CASSCF level.*

	E (cm^{-1})	g_x	g_y	g_z	WFT
1	0.0	0.0	0.0	19.8	$0.99\|\pm15/2\rangle$
2	118.1	0.1	0.1	19.6	$0.38\|\pm1/2\rangle + 0.29\|\pm3/2\rangle + 0.17\|\pm5/2\rangle$
3	224.5	0.4	0.6	16.8	$0.92\|\pm13/2\rangle$
4	307.9	2.2	2.6	14.2	$0.22\|\pm11/2\rangle + 0.20\|\pm9/2\rangle + 0.19\|\pm7/2\rangle + 0.18\|\pm5/2\rangle + 0.15\|\pm3/2\rangle$
5	371.4	8.4	5.3	0.1	$0.51\|\pm11/2\rangle + 0.15\|\pm5/2\rangle + 0.13\|\pm7/2\rangle$
6	427.5	3.5	6.5	11.3	$0.47\|\pm9/2\rangle + 0.20\|\pm7/2\rangle + 0.15\|\pm11/2\rangle + 0.14\|\pm1/2\rangle$
7	542.3	0.4	0.6	16.9	$0.29\|\pm7/2\rangle + 0.28\|\pm5/2\rangle + 0.19\|\pm9/2\rangle + 0.17\|\pm3/2\rangle$
8	818.9	0.0	0.0	19.8	$0.37\|\pm1/2\rangle + 0.30\|\pm3/2\rangle + 0.19\|\pm5/2\rangle$

*Table S8: Computed energies levels (the ground state is set at zero), component values of the Lande factor g and wavefunction composition for each M_J state of the ground-state multiplet for the Dy center in the spiropyran form of **1-Dy** (gas phase optimized structure). Calculations carried out at the CASSCF level.*

	E (cm^{-1})	g_x	g_y	g_z	WFT
1	0.0	0.2	0.3	18.7	$0.86\|\pm15/2\rangle$
2	40.9	0.1	0.2	18.7	$0.22\|\pm9/2\rangle + 0.18\|\pm7/2\rangle + 0.17\|\pm5/2\rangle + 0.15\|\pm3/2\rangle + 0.13\|\pm1/2\rangle$
3	107.6	2.3	3.9	13.4	$0.52\|\pm13/2\rangle + 0.14\|\pm9/2\rangle + 0.12\|\pm5/2\rangle$
4	143.4	0.3	4.4	12.2	$0.38\|\pm11/2\rangle + 0.17\|\pm13/2\rangle + 0.14\|\pm9/2\rangle$
5	210.4	9.0	4.8	0.1	$0.33\|\pm7/2\rangle + 0.12\|\pm11/2\rangle + 0.12\|\pm1/2\rangle + 0.12\|\pm13/2\rangle + 0.12\|\pm5/2\rangle + 0.11\|\pm9/2\rangle$
6	308.6	1.9	4.5	10.5	$0.27\|\pm9/2\rangle + 0.22\|\pm5/2\rangle + 0.17\|\pm11/2\rangle + 0.14\|\pm13/2\rangle$
7	393.4	1.3	3.3	14.2	$0.24\|\pm5/2\rangle + 0.24\|\pm3/2\rangle + 0.21\|\pm7/2\rangle + 0.11\|\pm1/2\rangle$
8	603.0	0.0	0.1	19.2	$0.48\|\pm1/2\rangle + 0.30\|\pm3/2\rangle + 0.12\|\pm5/2\rangle$

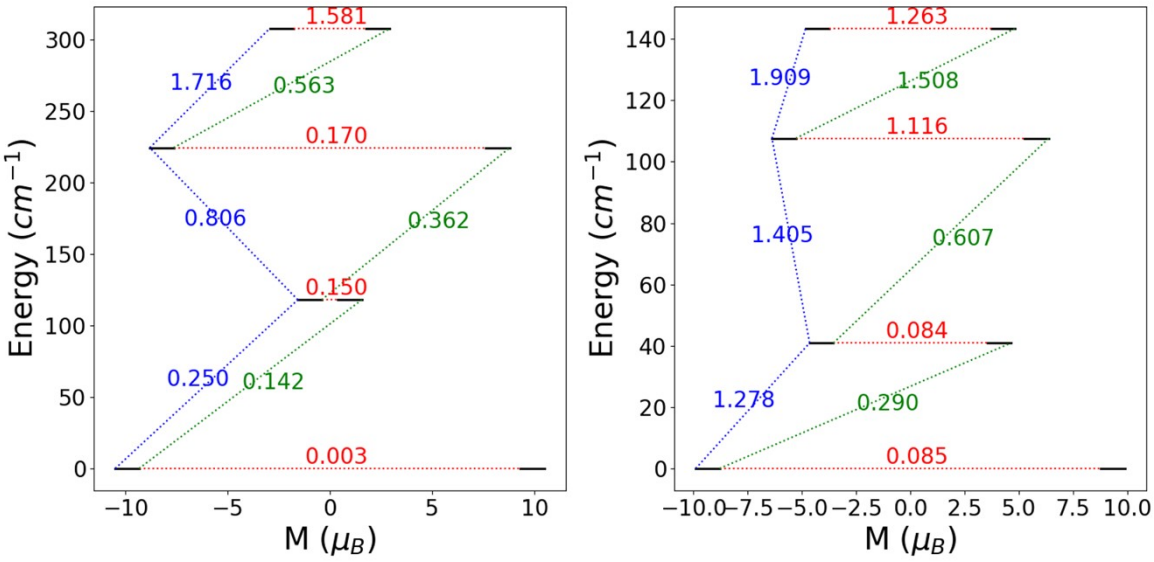


*Figure S43: Energies (in cm^{-1}) and projected μz (in μB) values along the ground magnetic axis for the merocyanine (left) and spiropyran (right) forms of **1Dy**. Black lines represent the four lowest Kramers doublets of each complex. The values of the magnetic (i.e. isotropic Zeeman) transition moments between the states are given for comparison. The values in red correspond to QTM (for the GS) and TA-QTM (for the ESs) mechanisms of the magnetization relaxation, whereas blue and green values correspond to Orbach mechanisms.*

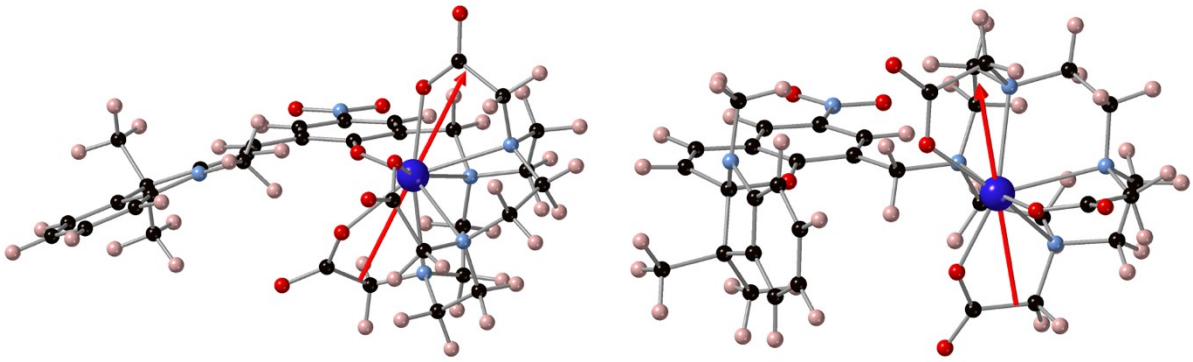


*Figure S44: Anisotropy axes of the Dy(III) ions for the merocyanine (left) and spiropyran (right) forms of **1Dy**.*

Références

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