

Electronic Supplementary Information

**A High Fatigue Resistant Photoswitchable Fluorescent Spiropyran -
Polyoxometalate-BODIPY Single-Molecule**

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S1 Synthetic procedures

Chemicals and reagents. All available chemicals were purchased from major chemical suppliers and used as received. The Anderson-type polyoxomolybdate $(\text{TBA})_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{S1}$, the SP-POM-NH₂ hybrid^{S2} and the alkyne-functionalized BODIPY^{S3} have been synthesized as previously described.

Elemental analyses were performed by the Service de Microanalyse of CNRS, 91198 Gif sur Yvette, France. Infrared spectra (ATR) were recorded on an IRFT Nicolet 6700 apparatus. Relative intensities are given after the wavenumber as vs = very strong, s = strong, m = medium, w = weak, sh. = shoulder, br. = broad. NMR spectra were recorded on a Bruker Advance 300 spectrometer operating at 300 MHz for ¹H and 75 MHz for ¹³C nuclei. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; br, broad peaks; m, multiplet or overlapping peaks.

Synthesis of $(\text{TBA})_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNHC}(\text{O})\text{CH}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-N}_3\}_2]$ (Azido-POM-Azido)

To a solution of $(\text{TBA})_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ (370 mg, 0.20 mmol) in CH₃CN (10 mL) were added 3-(4-azidophenyl)propionic acid (150 mg, 0.78 mmol) and EEDQ (280 mg, 1.13 mmol). The reaction mixture was stirred at room temperature during one week. The solvent was removed under vacuum and the residue was dissolved in a minimum of CH₃CN. The solution was added to a large quantity of Et₂O (30 mL). The resulting precipitate was then isolated by filtration. This treatment was repeated three times. The **Azido-POM-Azido** hybrid (303 mg, 0.14 mmol) was isolated as a pale beige solid in 68% yield.

¹H NMR (CD₃CN, 300 MHz, 298K) δ 65.13 (s, br, 12H, -CH₂-O), 7.26 (d, 4H, H_{aro}), 7.00 (d, 4H, H_{aro}, J = Hz), 6.37 (br, 2H, NH), 3.13 (m, 24H, -NCH₂- (TBA)), 2.83 (br, 4H, -CH₂CO-), 2.71 (br, 4H, -CH₂-), 1.63 (m, 24H, -NCH₂CH₂- (TBA)), 1.38 (m, 24H, -NCH₂CH₂CH₂- (TBA)), 0.98 (m, 36H, -CH₃ (TBA)).

¹³C NMR (CD₃CN, 75 MHz, 298K) δ 173.0, 138.4, 137.7, 130.2, 119.1, 58.4, 36.1, 31.1, 23.5, 19.8, 13.3.

IR (ATR) : ν (cm⁻¹) 3287 (w), 3068 (w), 2960 (ν C-H, m), 2933 (ν C-H, m), 2872 (ν C-H, m), 2100 (ν N₃, s), 1672 (ν C=O, s), 1552 (m), 1504 (m), 1480 (m), 1468 (m), 1379 (w), 1287

(m), 1106 (w), 1056 (m), 1019 (m), 938 (v Mo=O, vs), 916 (v Mo=O, vs), 899 (v Mo=O, vs), 813 (w), 651 (v Mo-O-Mo, vs, br), 560 (w), 532 (w).

Anal. Calcd for $\text{MnMo}_6\text{O}_{26}\text{C}_{74}\text{H}_{138}\text{N}_{11}$ (2228.5): C, 39.88; H, 6.24; N, 6.91. Found : C, 38.89; H, 6.24; N, 6.67.

Synthesis of $(\text{TBA})_{2.4}\text{Cu}_{0.6}[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNHC}(\text{O})\text{CH}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-N}_3\text{C}_2\text{H-CH}_2\text{-O-C}_6\text{H}_4\text{-C}_{17}\text{H}_{22}\text{N}_2\text{BF}_2\}_2]$ (BODIPY-POM-BODIPY)

To a solution of **Azido-POM-Azido** (350 mg, 0.16 mmol) and alkyne-functionalized BODIPY (273 mg, 0.63 mmol) in acetonitrile (5 mL) were added Cu^0 (25 mg, 0.39 mmol) and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (59 mg, 0.16 mmol). The reaction mixture was stirred at room temperature during 4 days. The suspension was then filtered through a pad of Celite and the filtrate added to a large quantity of Et_2O (40 mL). The resulting precipitate was then isolated by filtration, dissolved in a minimum of CH_3CN and added again to a large quantity of Et_2O . This treatment was repeated twice. **BODIPY-POM-BODIPY** (160 mg, 0,05 mmol) was isolated as a red solid (yield 33%).

^1H NMR (CD_3CN , 300 MHz, 298K) δ 65.04 (s, br, 12H, $-\text{CH}_2\text{-O}$), 8.51 (s, 2H, triazolyl-H), 7.71 (d, 4H, H_{aro}), 7.43 (d, 4H, H_{aro}), 7.27 (br, 8H, H_{aro}), 6.37 (br, 2H, NH), 5.35 (d, 4H, $\text{O-CH}_2\text{-}$), 3.12 (m, 19.2H, $-\text{NCH}_2\text{-}$ (TBA)), 2.93 (br, 4H, $-\text{CH}_2\text{CO-}$), 2.76 (br, 4H, $-\text{CH}_2\text{-}$), 2.48 (s, 12H, CH_3), 2.33 (q, 8H, $-\text{CH}_2\text{-CH}_3$), 1.62 (m, 19.2H, $-\text{NCH}_2\text{CH}_2\text{-}$ (TBA)), 1.36 (m, 31.2H, 19.2H $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{-}$ (TBA) + 12H $-\text{CH}_3$), 0.98 (m, 40.8H, 28.8H $-\text{CH}_3$ (TBA) + 12H $-\text{CH}_2\text{-CH}_3$).

^{13}C NMR (CD_3CN , 75 MHz, 298K) δ 173.1, 158.9, 153.4, 142.5, 140.9, 138.9, 135.4, 133.0, 130.9, 130.4, 129.6, 127.8, 121.2, 116.8, 115.8, 61.8, 58.4, 36.0, 31.5, 23.5, 19.7, 16.6, 14.0, 13.2, 11.8, 11.3.

IR (ATR) : ν (cm^{-1}) 3287 (w), 3068 (w), 2961 (v C-H, m), 2931 (v C-H, m), 2871 (v C-H, m), 1672 (v C=O, s), 1538 (m), 1473 (m), 1405 (w), 1379 (w), 1317 (m), 1237 (w), 1190 (s), 1110 (m), 1050 (m), 979 (m), 940 (v Mo=O, vs), 915 (v Mo=O, vs), 899 (v Mo=O, vs), 836 (m), 654 (v Mo-O-Mo, vs, br), 559 (w), 532 (w).

Anal. Calcd for $\text{MnMo}_6\text{O}_{28}\text{C}_{116.4}\text{H}_{174.4}\text{N}_{14.4}\text{B}_2\text{F}_4\text{Cu}_{0.6}$ (2989.87): C, 46.76; H, 5.88; N, 6.75. Found : C, 45.81; H, 5.78; N, 6.47. The presence of copper was detected by EDX.

Synthesis of (TBA)₃[MnMo₆O₁₈{(OCH₂)₃CNHC(O)CH₂-CH₂-C₆H₄-N₃}] {(OCH₂)₃CNHC(O)C₂₀H₁₉N₂O₃}] (SP-POM-Azido)

To a solution of SP-POM-NH₂ (400 mg, 0.18 mmol) in CH₃CN (5 mL), 3-(4-azidophenyl) propionic acid (102 mg, 0.53 mmol) and EEDQ (158 mg, 0.64 mmol) were added. The reaction mixture was stirred at room temperature during one week. The solution was added to a large quantity of Et₂O (80 mL). The resulting precipitate was then isolated by filtration. This treatment was repeated three times. The **SP-POM-Azido** hybrid (350 mg, 0.14 mmol) was isolated in 80 % yield.

¹H NMR (CD₃CN, 300 MHz, 298K) δ 65.46 (s, br, 12H, -CH₂-O), 8.05 (m, 2H, H_{SP}), 7.26-7.09 (m, 5H, 2H_{azide} + 3H_{SP}), 6.99 (d, 2H, H_{azide}), 6.84 (t, 1H, H_{SP}), 6.70 (2H, H_{SP}), 6.41 (br, 2H, NH), 5.89 (d, 1H, H_{SP}), 3.49 (br, 1H, H_{SP}), 3.32 (br, 1H, H_{SP}), 3.12 (m, 24H, -NCH₂- (TBA)), 2.82-2.71 (m, 6H, 4H_{azide} + 2H_{SP}), 1.62 (m, 24H, -NCH₂CH₂- (TBA)), 1.36 (m, 24H, -NCH₂CH₂CH₂- (TBA)), 1.24 (s, 3H, H_{SP}), 1.13 (s, 3H, H_{SP}), 0.97 (m, 36H, -CH₃ (TBA)).

¹³C NMR (CD₃CN, 75 MHz, 298K) δ 172.9 (C_{Azide}), 172.2 (C_{SP}), 159.4 (C_{SP}), 146.7 (C_{SP}), 141.1 (C_{SP}), 138.4 (C_{Azide}), 137.7 (C_{Azide}), 136.1 (C_{SP}), 130.1 (C_{Azide}), 128.9 (C_{SP}), 127.8 (C_{SP}), 125.6 (C_{SP}), 123.5 (C_{SP}), 122.9 (C_{SP}), 121.7 (C_{SP}), 119.4 (C_{SP}), 119.1 (C_{Azide}), 119.1 (C_{SP}), 115.4 (C_{SP}), 107.2 (C_{SP}), 107.1 (C_{SP}), 58.4 (C_{TBA}), 52.6 (C_{SP}), 40.7 (C_{SP}), 36.1 (C_{Azide}), 33.8 (C_{SP}), 31.1 (C_{Azide}), 26.1 (C_{SP}), 23.5 (C_{TBA}), 19.8 (C_{TBA}), 19.1 (C_{SP}), 13.3 (C_{TBA}).

IR (ATR) : ν (cm⁻¹) 3289 (w), 3063 (w), 2960 (ν C-H, m), 2934 (ν C-H, m), 2872 (ν C-H, m), 2100 (ν N₃, s), 1673 (ν C=O, s), 1610 (m), 1575 (w), 1552 (m), 1507 (m), 1480 (m), 1459 (m), 1379 (w), 1333 (m), 1274 (m), 1158 (w), 1112 (w), 1087 (w), 1060 (m), 1022 (m), 939 (ν Mo=O, vs), 917 (ν Mo=O, vs), 900 (ν Mo=O, vs), 808 (m), 747 (m), 653 (ν Mo-O-Mo, vs, br), 562 (m).

Anal. Calcd for MnMo₆O₂₉C₈₆H₁₄₉N₁₀ (2417.76): C, 42.72; H, 6.21; N, 5.79. Found: C, 41.93; H, 6.18; N, 5.47.

Synthesis of (TBA)_{2.4}Cu_{0.6}[MnMo₆O₁₈{(OCH₂)₃CNHC(O)CH₂-CH₂-C₆H₄-N₃C₂H-CH₂-O-C₆H₄-C₁₇H₂₂N₂BF₂}] {(OCH₂)₃CNHC(O)C₂₀H₁₉N₂O₃}] (SP-POM-BODIPY)

To a solution of **SP-POM-Azido** (250 mg, 0.10 mmol) and alkyne-functionalized BODIPY (89 mg, 0.20 mmol) in acetonitrile (4 mL) were added Cu⁰ (6.5 mg, 0.10 mmol) and [Cu(CH₃CN)₄]PF₆ (19.5 mg, 0.05 mmol). The reaction mixture was stirred at room

temperature during 4 days. The suspension was then filtered through a pad of Celite and the filtrate was added to a large quantity of Et₂O (50 mL). The resulting precipitate was then isolated by filtration, dissolved in a minimum of CH₃CN and added again to a large quantity of Et₂O. This treatment was repeated twice. **SP-POM-BODIPY** (250 mg, 0.09 mmol) was isolated as a red powder (yield 90%).

¹H NMR (CD₃CN, 300 MHz, 298K) δ 65.40 (s, br, 12H, -CH₂-O), 8.54 (s, 1H, H_{BODIPY}), 8.05 (s, 1H, H_{SP}), 8.01 (s, 1H, H_{SP}), 7.71 (d, 2H, H_{BODIPY}), 7.44 (d, 2H, H_{BODIPY}), 7.27 (s, 4H, H_{BODIPY}), 7.12 (m, 3H, H_{SP}), 6.84 (t, 1H, H_{SP}), 6.70 (m, 2H, H_{SP}), 6.42 (br, 2H, NH), 5.89 (d, 1H, H_{SP}), 5.35 (d, 2H, H_{BODIPY}), 3.51 (br, 1H, H_{SP}), 3.35 (br, 1H, H_{SP}), 3.12 (m, 19.2H, -NCH₂- (TBA)), 2.94 (br, 2H, H_{BODIPY}), 2.77 (m, 4H, 2H_{BODIPY} + 2H_{SP}), 2.48 (s, 6H, H_{BODIPY}), 2.33 (q, 4H, H_{BODIPY}), 1.62 (m, 19.2H, -NCH₂CH₂- (TBA)), 1.36 (m, 25.2H, 19.2 H -NCH₂CH₂CH₂- (TBA) + 6 H_{BODIPY}), 1.23 (s, 3H, H_{SP}), 1.13 (s, 3H, H_{SP}), 0.97 (m, 34.8H, 28.8H -CH₃ (TBA) + 6 H_{BODIPY}).

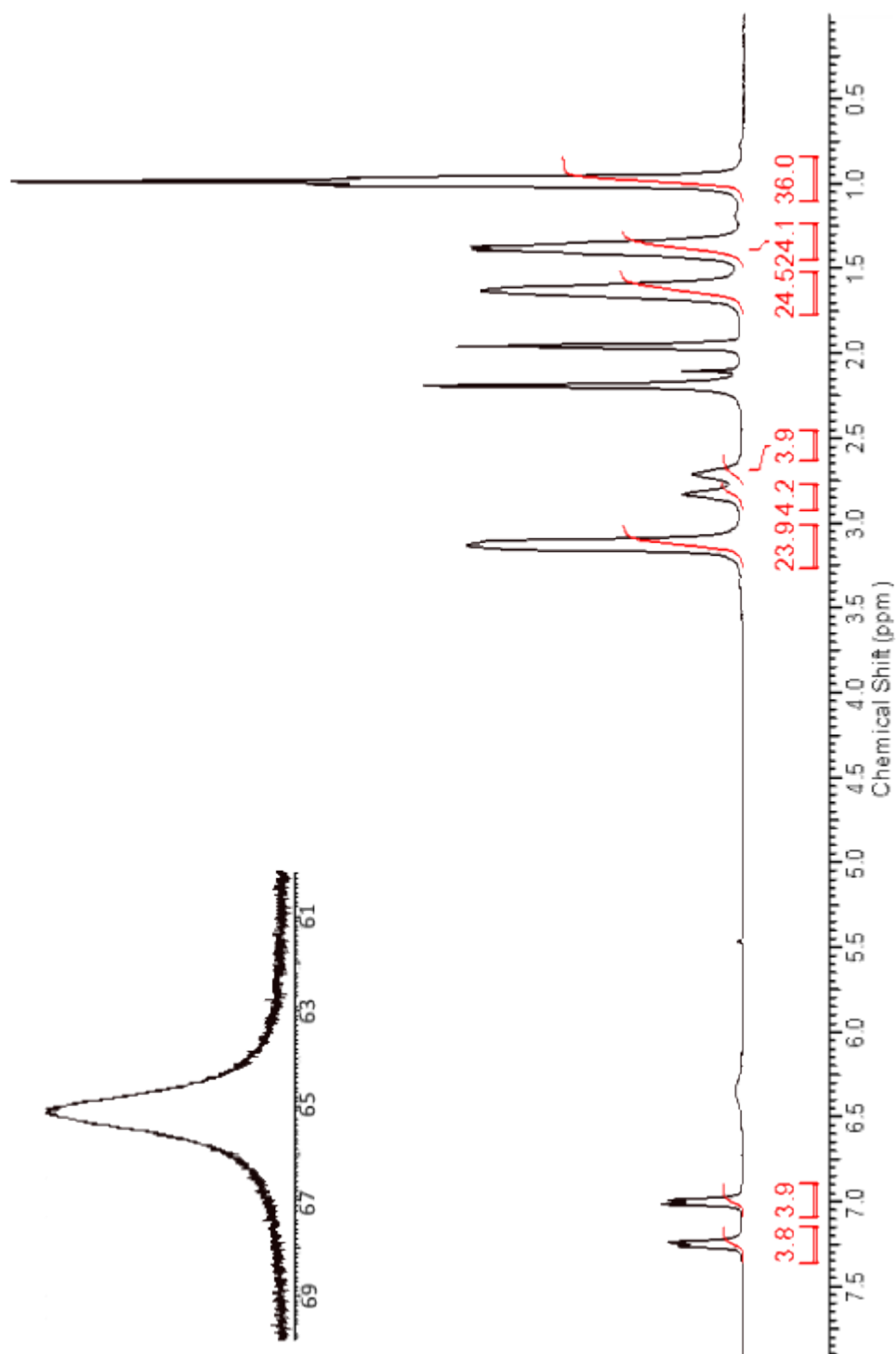
¹³C NMR (CD₃CN, 75 MHz, 298K) δ 173.1 (C_{BODIPY}), 172.3 (C_{SP}), 159.4, 158.9 (C_{BODIPY}), 153.4 (C_{BODIPY}), 146.8 (C_{SP}), 142.5 (C_{BODIPY}), 141.0 (C_{SP}), 140.9 (C_{BODIPY}), 138.9 (C_{BODIPY}), 136.1 (C_{SP}), 135.3 (C_{BODIPY}), 132.9 (C_{BODIPY}), 130.9 (C_{BODIPY}), 130.4 (C_{BODIPY}), 129.6 (C_{BODIPY}), 128.9 (C_{SP}), 127.8 (C_{BODIPY}), 125.6 (C_{SP}), 123.6 (C_{SP}), 122.9 (C_{SP}), 121.7 (C_{SP}), 121.1 (C_{BODIPY}), 119.4 (C_{SP}), 119.1 (C_{SP}), 115.8 (C_{BODIPY}), 115.4 (C_{SP}), 107.2 (C_{SP}), 107.1 (C_{SP}), 61.8 (C_{BODIPY}), 58.4 (C_{TBA}), 52.6 (C_{SP}), 40.8 (C_{SP}), 35.9 (C_{BODIPY}), 33.8 (C_{SP}), 31.5 (C_{BODIPY}), 26.1 (C_{SP}), 23.5 (C_{TBA}), 19.8 (C_{TBA}), 19.1 (C_{SP}), 16.6 (C_{BODIPY}), 14.0 (C_{BODIPY}), 13.3 (C_{TBA}), 11.8 (C_{BODIPY}), 11.3 (C_{BODIPY}).

IR (ATR) : ν (cm⁻¹) 3289 (w), 3068 (w), 2960 (v C-H, m), 2932 (v C-H, m), 2872 (v C-H, m), 1675 (v C=O, s), 1608 (w), 1540 (m), 1516 (m), 1477 (m), 1460 (m), 1405 (w), 1379 (w), 1321 (m), 1273 (m), 1192 (s), 1114 (w), 1058 (m), 1024 (m), 980 (m), 940 (v Mo=O, vs), 918 (v Mo=O, vs), 901 (v Mo=O, vs), 809 (w), 747 (m), 657 (v Mo-O-Mo, vs, br), 561 (m), 534 (m).

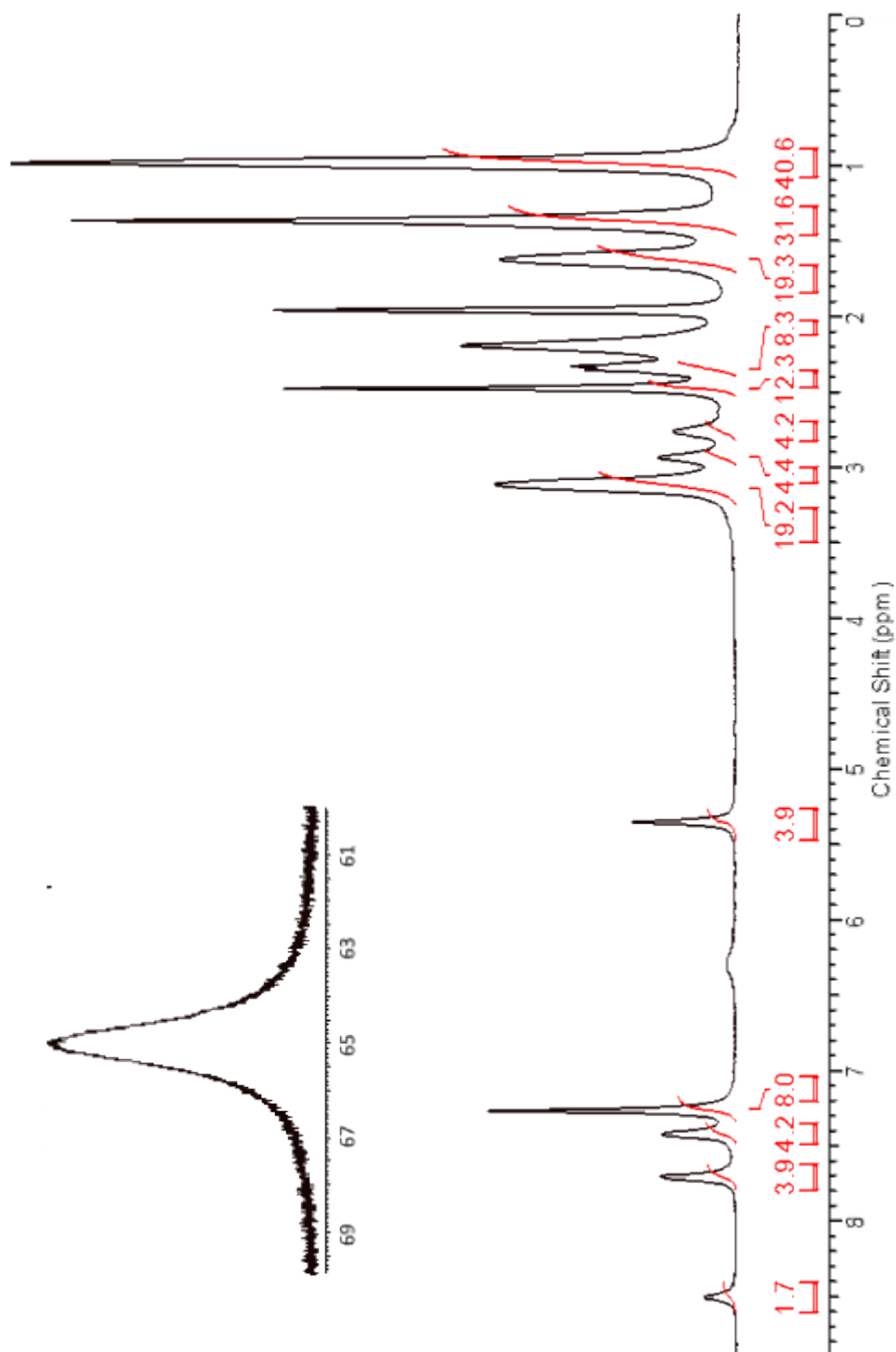
Anal. Calcd for MnMo₆O₃₀C_{102.4}H_{156.4}N_{11.4}BF₂Cu_{0.6} (2744.74): C, 44.81; H, 5.74; N, 5.82. Found : C, 43.86 ; H, 5.71; N, 5.47. The presence of copper was detected by EDX.

S2 Solution ^1H NMR

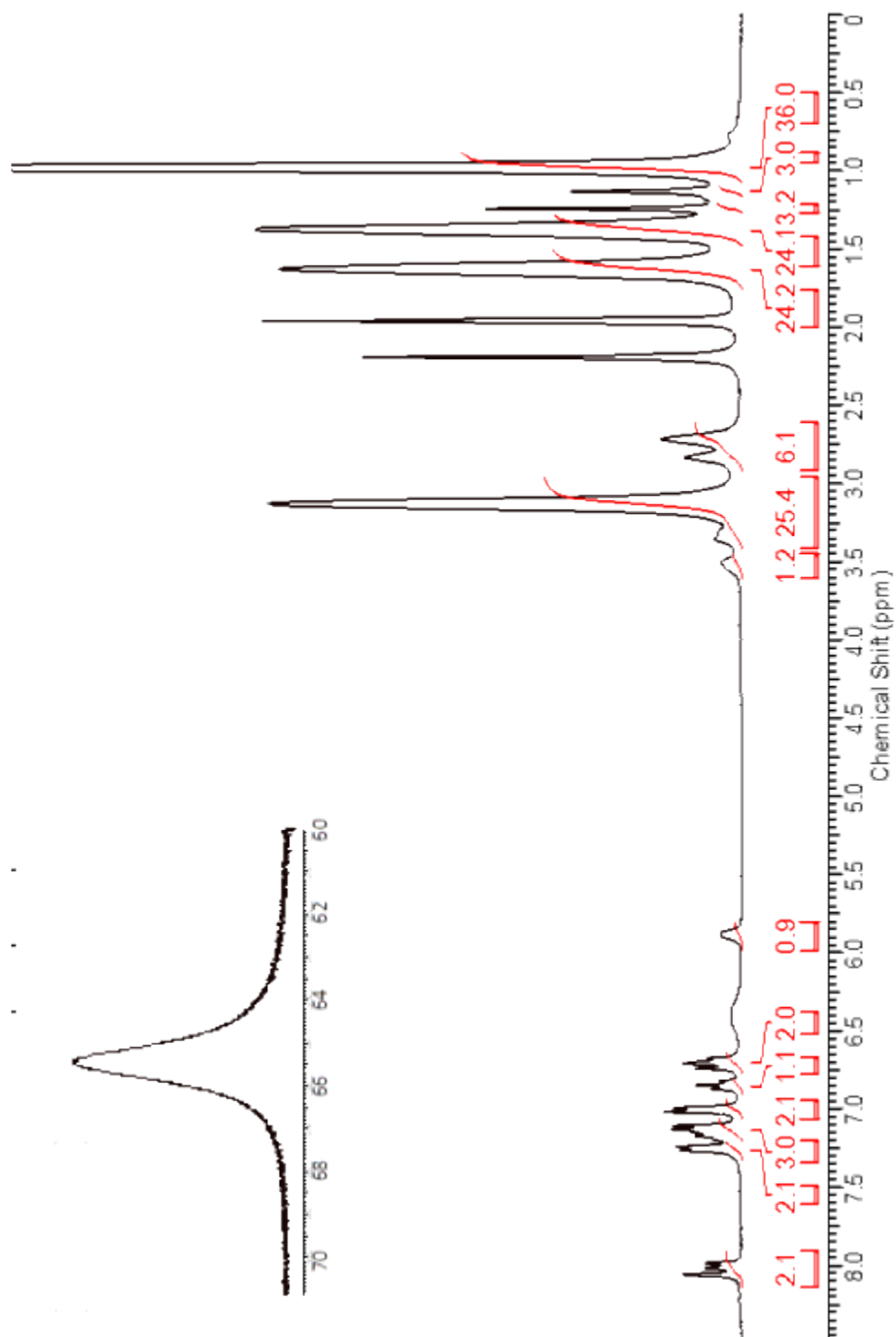
^1H NMR (CD_3CN) spectrum of Azido-POM-Azido in the 0-8 ppm range. Inset : peak in the 60-70 ppm range.



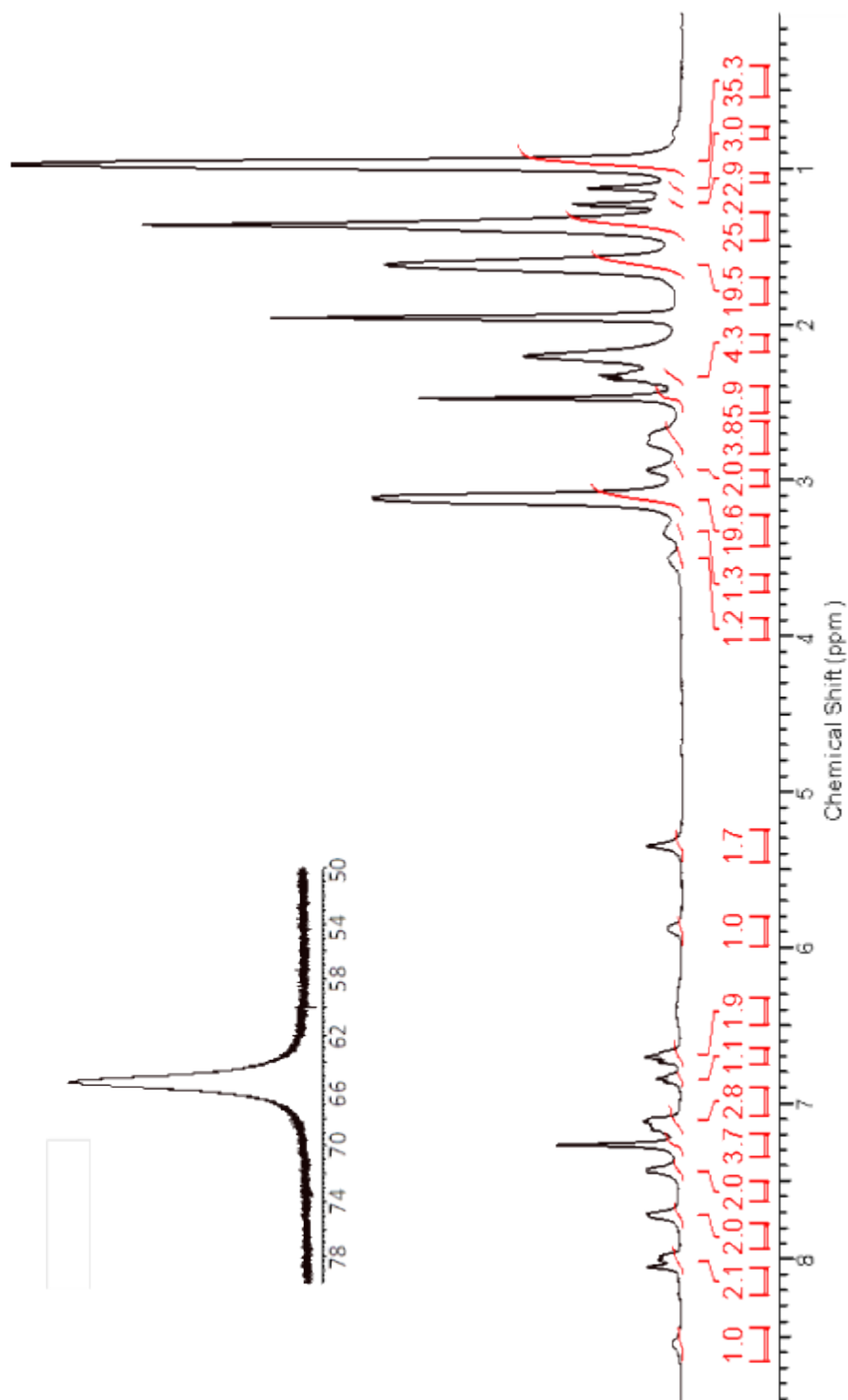
^1H NMR (CD_3CN) spectrum of **BODIPY-POM-BODIPY** in the 0-9 ppm range. Inset : peak in the 60-70 ppm range.



^1H NMR (CD_3CN) spectrum of **SP-POM-Azido** in the 0-8.5 ppm range. Inset: peak in the 60-71 ppm range.

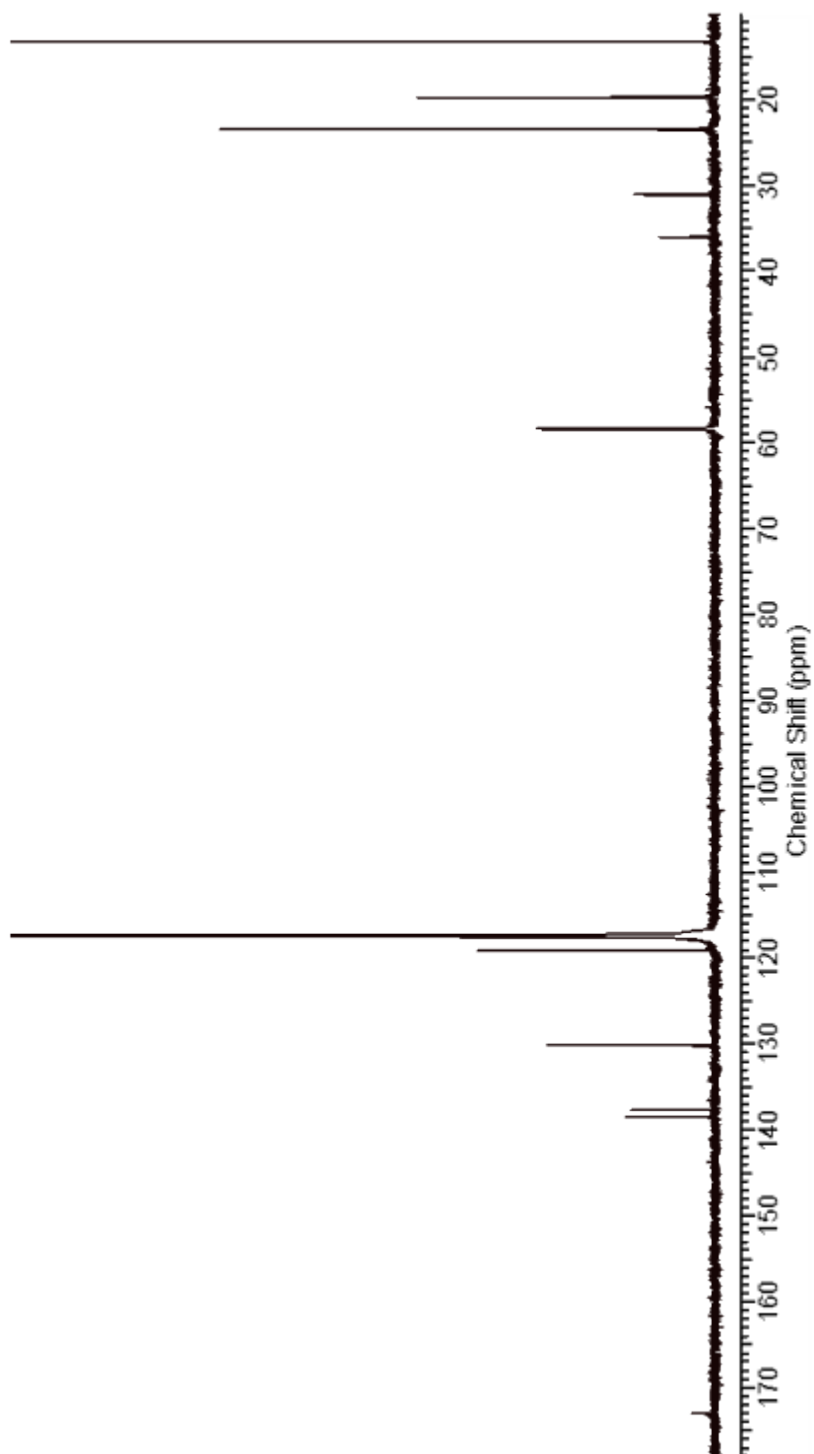


^1H NMR (CD_3CN) spectrum of **SP-POM-BODIPY** in the 0-9 ppm range. Inset: peak in the 50-80 ppm range.

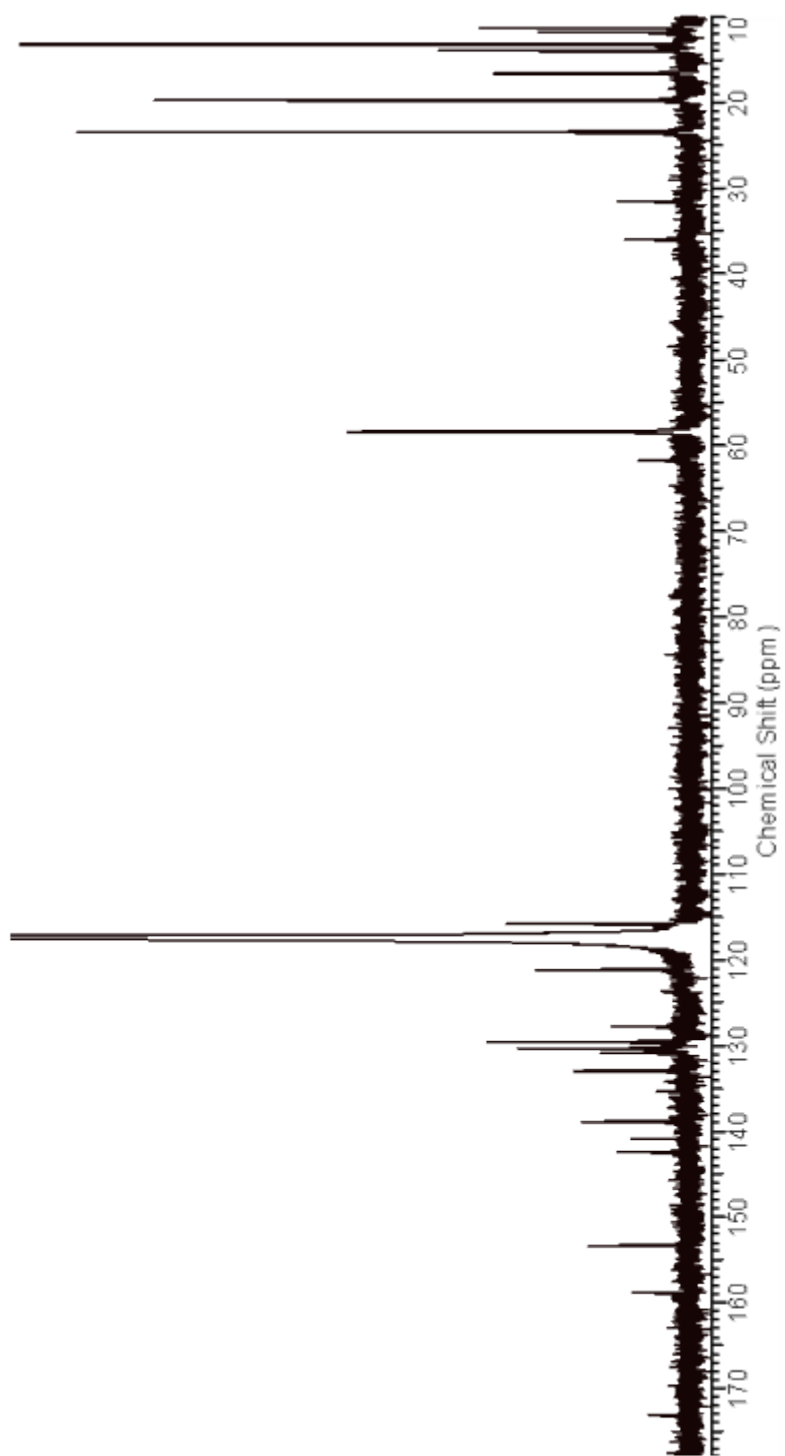


S3 Solution ^{13}C NMR

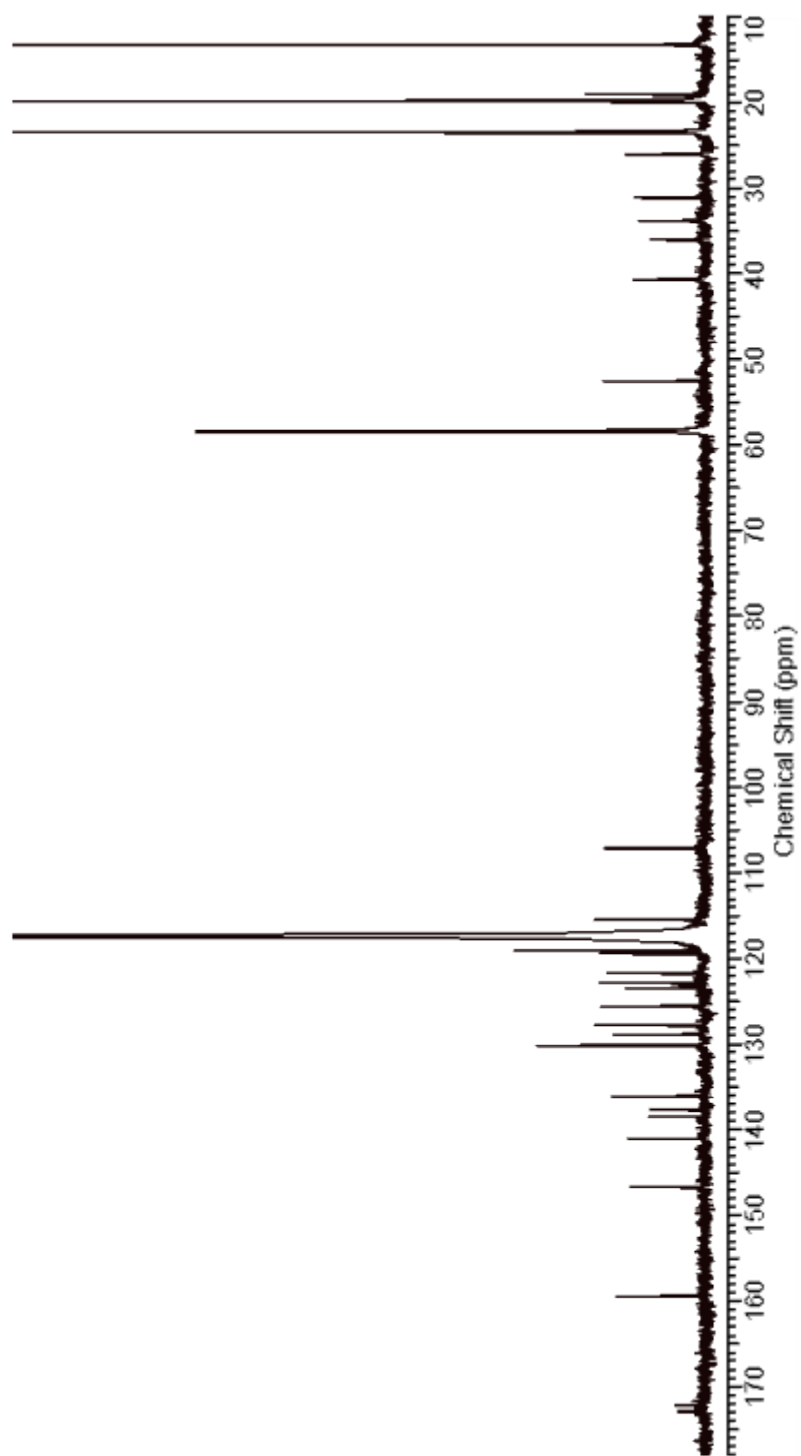
^{13}C NMR (CD_3CN) spectrum of Azido-POM-Azido.



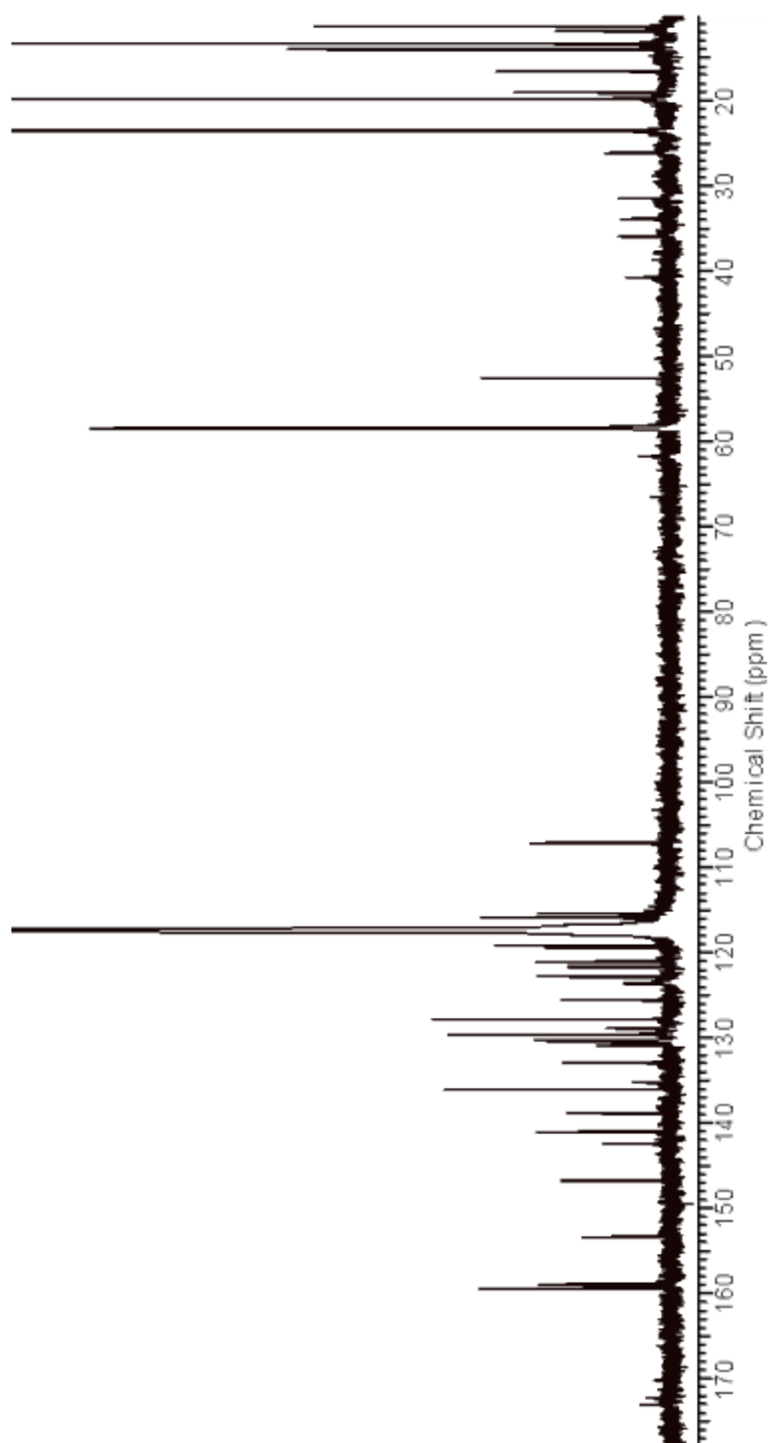
^{13}C NMR (CD_3CN) spectrum of **BODIPY-POM-BODIPY**.



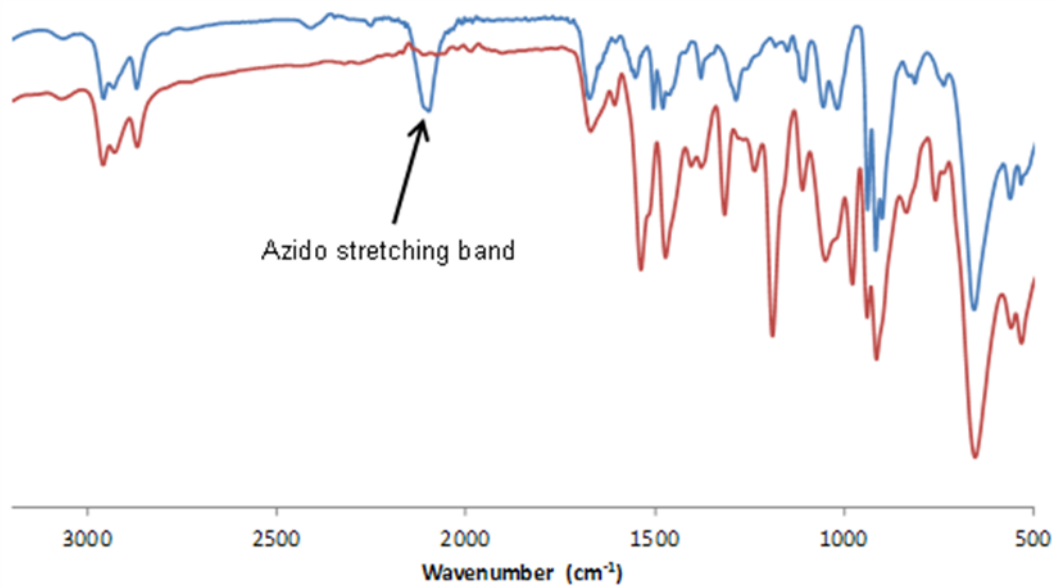
^{13}C NMR (CD_3CN) spectrum of **SP-POM-Azido**



^{13}C NMR (CD_3CN) spectrum of **SP-POM-BODIPY**.



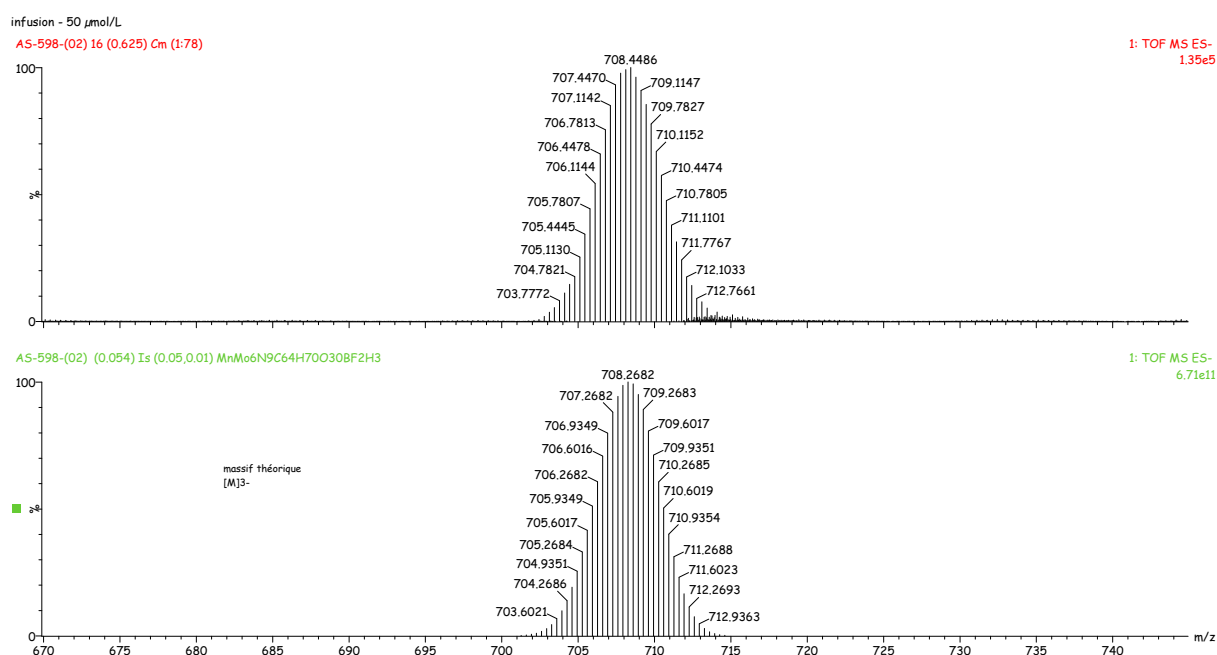
S4 Infrared spectra



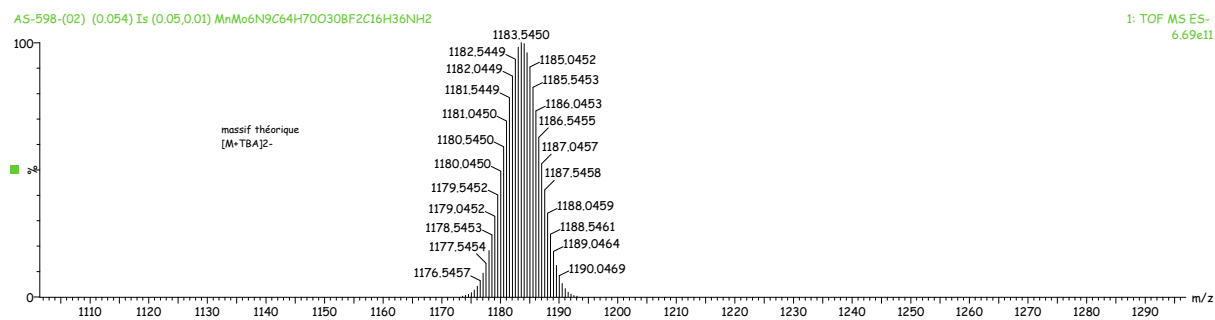
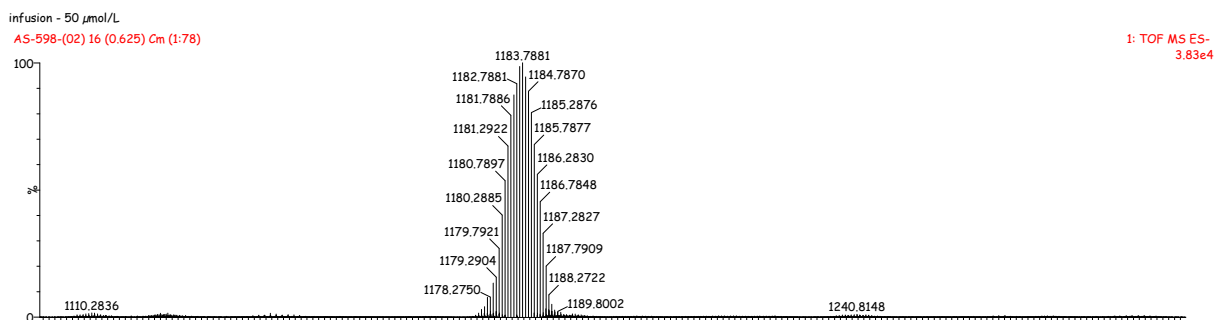
Infrared spectra of Azido-POM-Azido (blue line) and BODIPY-POM-BODIPY (red line)

S5 ESI/MS Spectra of SP-POM-BODIPY

Electrospray ionization (ESI) mass spectra were recorded on a Xevo QToF WATERS (quadrupole-time-of-flight) instrument. The temperature of the source block was set to 120 °C, and the desolvation temperature to 200 °C. A capillary voltage of 1 kV was used in the negative scan mode, and the cone voltage was set to 10 V to control the extent of fragmentation of the identified species. Mass calibration was performed using a solution of sodium formate in water:acetonitrile (2:8) from m/z 50 to 3000. Sample solutions 50 $\mu\text{mol/L}$ in acetonitrile were injected via syringe pump directly connected to the ESI source at a flow rate of 20 $\mu\text{L}/\text{min}$.



Top: Experimental spectrum, bottom: simulated spectrum (related to $[\text{M}]^{3-}$ signal)



Top: Experimental spectrum, bottom: simulated spectrum (related to $[M+TBA]^{2-}$ signal)

Composition	Formula	Calculated	Observed
$[M]^{3-}$	$\text{MnMo}_6\text{O}_{30}\text{C}_{64}\text{N}_9\text{H}_{70}\text{BF}_2$	708.2682	708.4486
$[M+TBA]^{2-}$	$\text{MnMo}_6\text{O}_{30}\text{C}_{80}\text{N}_{10}\text{H}_{106}\text{BF}_2$	1183.5450	1183.7881

S6 Optical measurements

Diffuse reflectance spectra were collected at room temperature on a finely ground sample with a Cary 5G spectrometer (Varian) equipped with a 60 mm diameter integrating sphere and computer control using the “Scan” software. Diffuse reflectance was measured from 250 to 1550 nm with a 2 nm step using Halon powder (from Varian) as reference (100% reflectance). The reflectance data were treated by a Kubelka-Munk transformation^{S4} to better locate the absorption thresholds. The samples were irradiated with a Fisher Bioblock labosi UV lamp ($\lambda_{\text{exc}} = 365$ nm, $P = 6$ W). UV-vis absorption spectra in solution were obtained with the same Cary 5G spectrometer (Varian). Photoluminescence spectra were recorded in aerated solutions on a Jobin-Yvon Fluorolog 3 fluorometer equipped with a CCD camera. Samples were dissolved in acetonitrile and placed in quartz cells with a path length of 1 cm.

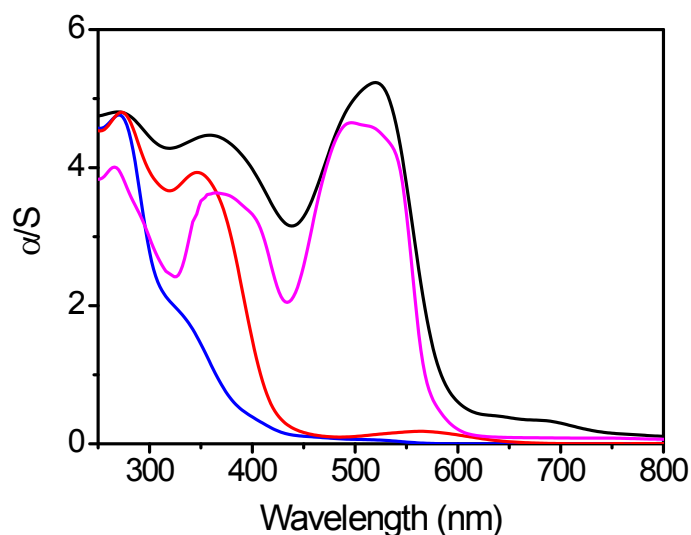


Figure S11: Normalized Kubelka-Munk transformed reflectivity spectra before UV irradiation of microcrystalline powders of **SP-POM-BODIPY** (—), **MnMo₆(tris)₂** (—), **SP-POM-NH₂** (—), and **BODIPY-POM-BODIPY** (—).

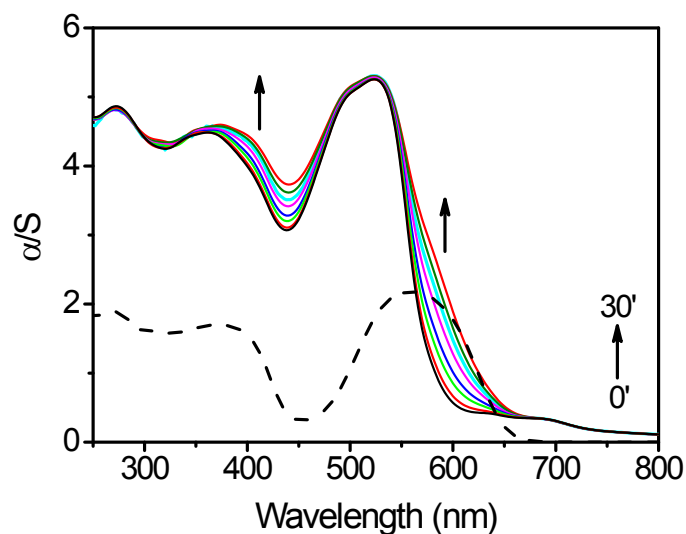


Figure SI2: Kubelka-Munk transformed reflectivity of **SP-POM-BODIPY** after 0, 0.333, 1, 2, 5, 6, 8, and 30 min of UV irradiation ($\lambda_{\text{ex}} = 365$ nm). The dotted line represents the absorption spectrum of **SP-POM-NH₂** after 30 min of UV irradiation displaying the broad absorption bands of the photogenerated MC form in the visible domain ($\lambda_{\text{max}} = 405$ and 570 nm).

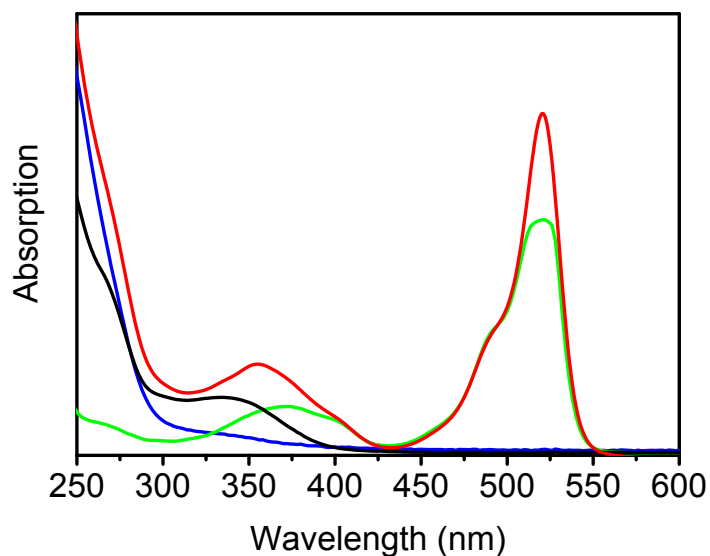


Figure SI3: Absorption spectra of **MnMo₆(tris)₂** (—), **SP-POM-NH₂** (—), **BODIPY-alkyne** (—) and **SP-POM-BODIPY** (—) in acetonitrile (10^{-5} M, 25°C).

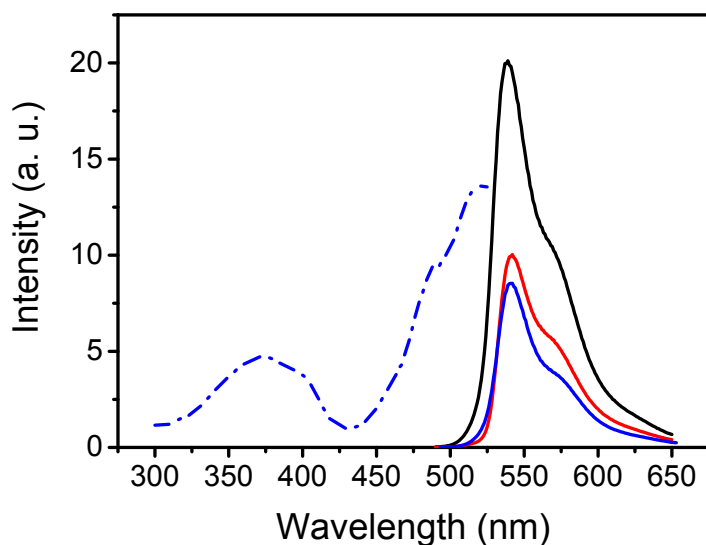


Figure SI4: Excitation spectrum of **SP-POM-BODIPY** (---) in acetonitrile (25°C, $\lambda_{\text{em}} = 534$ nm). Emission spectra of **BODIPY-alkyne** (—), **BODIPY-POM-BODIPY** (—) and **SP-POM-BODIPY** (—) in acetonitrile (10^{-5} M, 25°C, $\lambda_{\text{ex}} = 480$ nm).

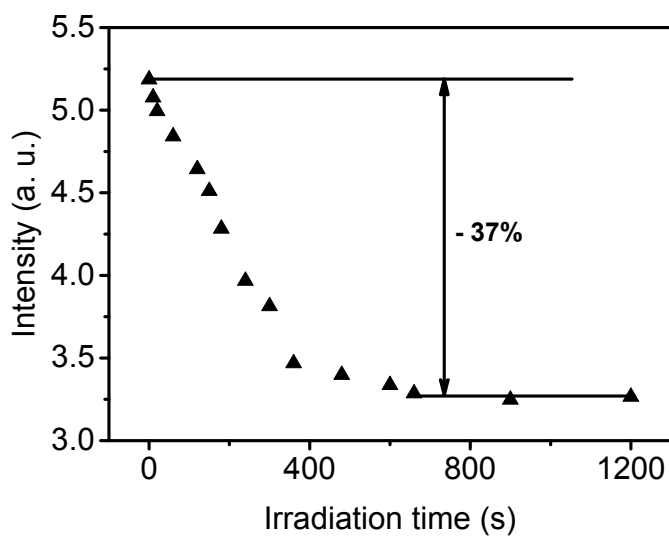


Figure SI5: Evolution of the maximum of the emission intensity located at 534 nm versus the 365 nm-UV irradiation time of **SP-POM-BODIPY** in acetonitrile (2.10^{-4} M, 25°C, $\lambda_{\text{ex}} = 480$ nm). The quenching reaches 37% of the intensity initial value at the photostationary state.

S7 References

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