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Functionalized polyoxometalates with intrinsic photochromic properties and their association with spiropyran cations

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Electronic Supplementary Information

Chemicals and reagents. All chemicals were used as purchased without purification. The alendronate ligand $AleH_4$[1] and the iodide salt of the spiropyran cation (SP)I[2] have been synthesized as previously described. The (SP)(NO_3) compound is prepared by mixing (SP)I (50 mg) and Ag(NO_3) (20 mg) in 10 mL of methanol, filtrating and evaporating.

Synthesis of $Na_6((C_2H_5)_2NH_2)_2[(Mo_3O_8)_4(O_3PC(C_3H_6NH_3)(O)PO_3)_4]\bullet 25H_2O$ (**1**). To 3.0 g of $Na_2MoO_4{\cdot}2H_2O$ (12.3 mmol) are added 1.08 g (4.3 mmol) of $AleH_4$. Concentrated hydrochloric acid is added dropwise until reaching pH = 3.0. The solution is let stirring for around 2 hours before 850 µL of diethylamine are added. 2M hydrochloric acid is added dropwise until reaching pH = 3.0 again and the clear, colourless solution is further let stirring for another hour before being left to evaporate at room temperature. Big colourless, hexagonal crystals are collected after one week. Yield 1.02 g (30% based on Mo). $^{31}P\ \{^1H\}$ NMR (δ, ppm): 19.9 (d, ^2J = 40.6 Hz); 24.8 (d, ^2J = 40.6 Hz). Anal. calc. for $Na_6C_{24}H_{110}N_6O_{85}P_8Mo_{12}$ (found): C 8.54 (8.71), H 3.28 (3.02), N 2.49 (2.40), P 7.33 (7.25), Mo 34.06 (34.06), Na 4.08 (4.41). IR (KBr pellets): ν (cm^{-1}) = 1506 (m), 1449 (m), 1392 (w), 1166 (s), 1128 (s), 1053 (s), 1026 (s), 920 (s), 885 (s), 796 (s), 691 (s), 661 (m), 644 (m), 557 (s). A deuterated sample of compound **1** has been prepared by dissolving 400 mg of **1** in 4 mL of D_2O, followed by evaporation to dryness under vacuum at 45 °C (45 mbar) of the resulting solution. This operation has been performed three times, leading to the compound **1-D**. The integrity of the POM fragment after the H-D exchange has been checked by ^{31}P NMR.

Synthesis of $Na_7(N(C_4H_9)_4)[(Mo_3O_8)_4(O_3PC(C_3H_6NH_3)(O)PO_3)_4]\bullet 43H_2O$ (**2**). $Na_2MoO_4{\cdot}2H_2O$ (500 mg, 2.07 mmol), $AleH_4$ (167 mg, 0.69 mmol) and $(C_4H_9)_4NBr$ (400 mg, 1.2 mmol) in 5mL of water were stirred and the pH adjusted to 3.2 by addition of a 4M HCl solution. The obtained mixture was sealed in a 23 mL Teflon-lined stainless steel reactor and heated to 130°C over a period of 4 h, kept at this temperature for 40 h, and cooled to room temperature over a period of 44 h. The resulting mixture was filtered and the filtrate left to

evaporate. Long white needles of **2** crystallize after a couple of hours. Yield 180 mg, 27% based on Mo. $^{31}P\ \{^1H\}$ NMR (δ, ppm): 19.8 (d, ^2J = 40.8 Hz); 24.8 (d) (d, ^2J = 40.8 Hz). Anal. calcd for $Na_7Mo_{12}C_{32}H_{158}N_5O_{103}P_8$ (%): C, 10.06; H 4.17; N 1.83; P 6.48; Mo 30.13; Na 4.21. Found: C, 10.54; H 4.17; N 1.87; P 6.18; Mo 30.10; Na 4.27. IR (KBr pellets): ν (cm^{-1}) = 1506 (m), 1469 (m), 1452 (m), 1397 (w), 1333 (w), 1169 (s), 1128 (s), 1051 (s), 1026 (vs), 964 (sh), 927 (vs), 884 (vs), 762 (s), 743 (w), 697 (s), 652 (s), 598 (w), 555 (s).

Synthesis of $Na(C_{20}N_2H_{23}O)_7[(Mo_3O_8)_4(O_3PC(C_3H_6NH_3)(O)PO_3)_4]\cdot 30H_2O$ (**3**). To a solution of 335 mg of **1** (0.10 mmol) in 5 mL of water is added a solution of 300 mg (0.81 mmol) of $(SP)(NO_3)$ in 25 mL of water. A yellowish-brown powder precipitates immediately; this suspension is let stirring for 15 min before being filtrated, washed with water and dried with ethanol and diethyl ether. Yield 260 mg (48% based on Mo). $^{31}P\ \{^1H\}$ NMR (δ, ppm): 19.9 (d, ^2J = 38.1 Hz); 25.3 (d, ^2J = 38.1 Hz). Anal. calc. for $NaC_{156}H_{257}N_{18}O_{97}P_8Mo_{12}$ (found): C 34.96 (35.72), H 4.83 (4.33), N 4.70 (4.84), P 4.62 (4.55), Mo 21.48 (21.32), Na 0.43 (0.45). IR (KBr pellets): ν (cm^{-1}) = 1486 (s), 1384 (w), 1362 (w), 1315 (sh), 1301 (m), 1161 (m), 1124 (m), 1053 (s), 1024 (s), 956 (w), 924 (s), 888 (s), 793 (s), 744 (w), 693 (s), 661 (m), 551 (m).

Room-temperature UV-visible diffuse reflectivity spectra were collected 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 reflectivity was measured from 250 to 1000 nm (i.e., from 4.96 to 1.24 eV) with a 2 nm step using Halon powder (from Varian) as a reference (100% reflectance). Samples **1-3** were irradiated with a Fisher Bioblock labosi UV lamp (λ_{exc} = 365 nm, P = 12 W).

X-ray crystallography. Intensity data collections were carried out with a Siemens SMART three-circle diffractometer for **1** and a Bruker Nonius X8 APEX 2 diffractometer for **2**, each equipped with a CCD bidimensional detector using the monochromatized wavelength λ(Mo

Kα) = 0.71073 Å. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program[3] based on the method of Blessing.[4] The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package.[5] Crystals of **2** rapidly loose water at room temperature. A single crystal of **2** was thus glued in Paraton-N oil and the data set collected at 100 K. In the structure of **1** and **2** there is a discrepancy between the formulae determined by elemental analysis and the formulae deduced from the crystallographic atom list because of the difficulty in locating all the disordered water molecules. Small "voids" are thus detected by checkcif. In the structure of **1**, one of the diethylammonium counter-ion is disordered over two positions and hydrogen atoms positions have not been determined on this molecule. **Elemental analysis** were performed by the Service Central d'Analyse of CNRS, 69390 Vernaison, France.

Infrared spectra (KBr pellets) were recorded on an IRFT Nicolet 550 apparatus.

References:

(1) V. Kubíček, J. Kotek, P. Hermann and I. Lukeš, *Eur. J. Inorg. Chem.*, 2007, 333.

(2) S. Bénard and P. Yu, *Adv. Mater.* 2000, **12**, 48.

(3) G. M. Sheldrick, SADABS, program for scaling and correction of area detector data, University of Göttingen, Germany, 1997.

(4) R. Blessing, *Acta Crystallogr.*, **1995**, *A51*, 33.

(5) Sheldrick, G. M. *SHELX-TL*, *Software Package for the Crystal Structure Determination*, version 5.03; Siemens Analytical X-ray Instrument Division: Madison, WI U.S.A., 1994.

	1	**2**
Chemical formula	$C_{24}H_{48}Mo_{12}N_6NaO_{65}P_8$	$C_{32}H_{72}Mo_{12}N_5Na_7O_{98}P_8$
M_r *(g.mol^{-1})*	2882.71	3654.92
Cell setting, space group	Tetragonal, $I4_1/a$	Tetragonal, I-4
Temperature (K)	293 (2)	100 (2)
a, b, c (Å)	19.7317 (12), 19.7317 (12), 29.047 (4)	19.6365 (15), 19.6365 (15), 15.5296 (13)
α, β, γ (°)	90.00, 90.00, 90.00	90.00, 90.00, 90.00
V (Å^3)	11309.0 (18)	5988.1 (8)
Z	4	2
D_x (Mg m^{-3})	1.693	2.027
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.48	1.46
Crystal form, colour	Parallelepiped, white	Parallelepiped, white
Crystal size (mm)	0.20 × 0.20 × 0.10	0.30 × 0.10 × 0.04
Diffractometer	CCDC area detector	Bruker APEX-II CCD
Data collection method	ϕ and ω scans	ϕ and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
T_{min}	0.756	0.668
T_{max}	0.866	0.944
No. of measured, independent and observed reflections	43623, 8382, 4096	199755, 8610, 8508
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.068	0.036
θ_{max} (°)	30.3	29.9
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR[F^2 > 2\sigma(F^2)]$, S	0.058, 0.187, 1.05	0.029, 0.086, 1.20
No. of reflections	8382 reflections	8610 reflections
No. of parameters	339	395
H-atom treatment	Constrained to parent site	Constrained to parent site
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.1248P)^2 + 50.9975P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.070P)^2 + 11.5114P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.147	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.14, –0.52	2.16, –2.39

[a] $R_1 = \frac{\Sigma\left|\,|F_o| - |F_c|\,\right|}{\Sigma|F_c|}$ [b] $wR_2 = \sqrt{\frac{\Sigma w(F_o^2 - F_c^2)^2}{\Sigma w(F_o^2)^2}}$

Tab. ESI1. Crystallographic data for complex **1** and **2**.

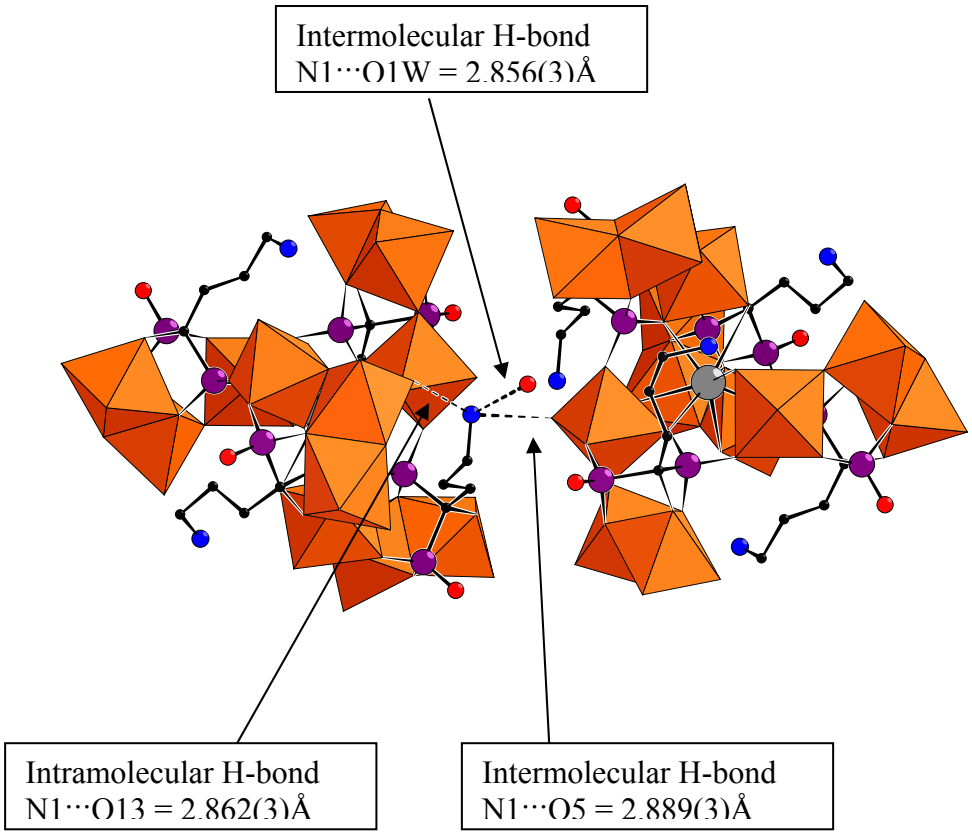

Fig . ESI1a : Details of the H-bond interactions between the nitrogen atom of the ligand and three surrounding oxygen atoms in **1** (the four nitrogen atoms of the POM are equivalent).

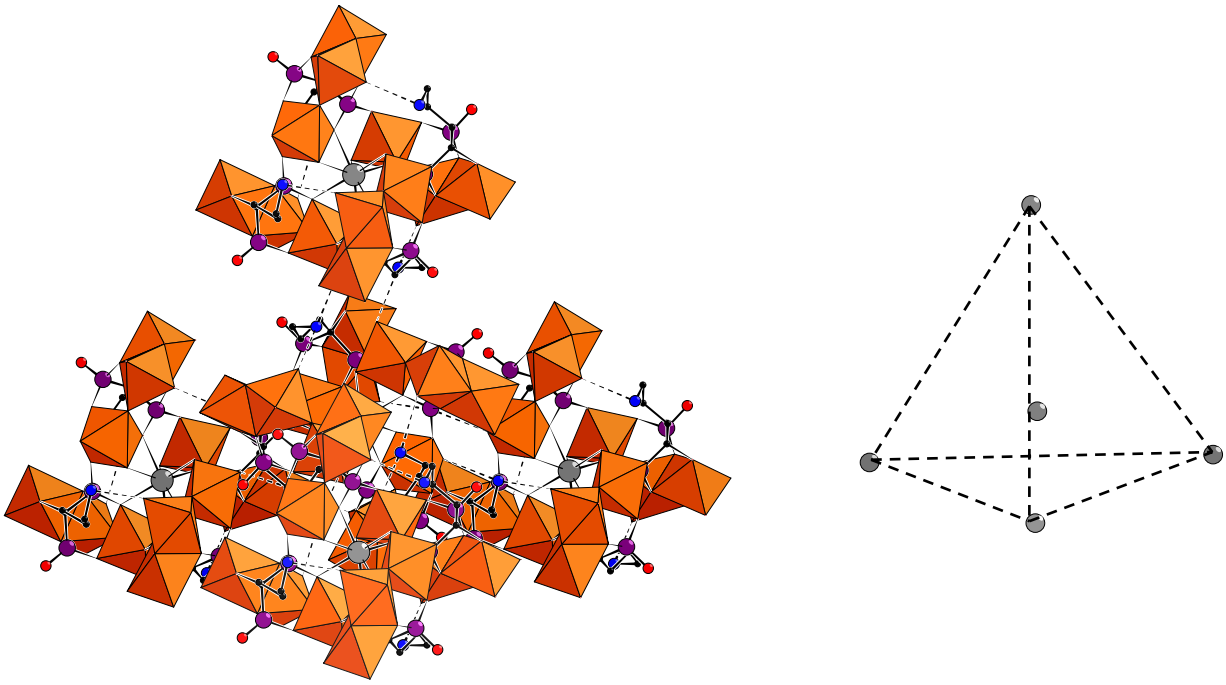

Fig . ESI1b : View of one POM and the four H-bonded neighbouring POMs in **1** and a scheme showing only the Na^+ positions to highlight the tetrahedral arrangement of the four POMs.

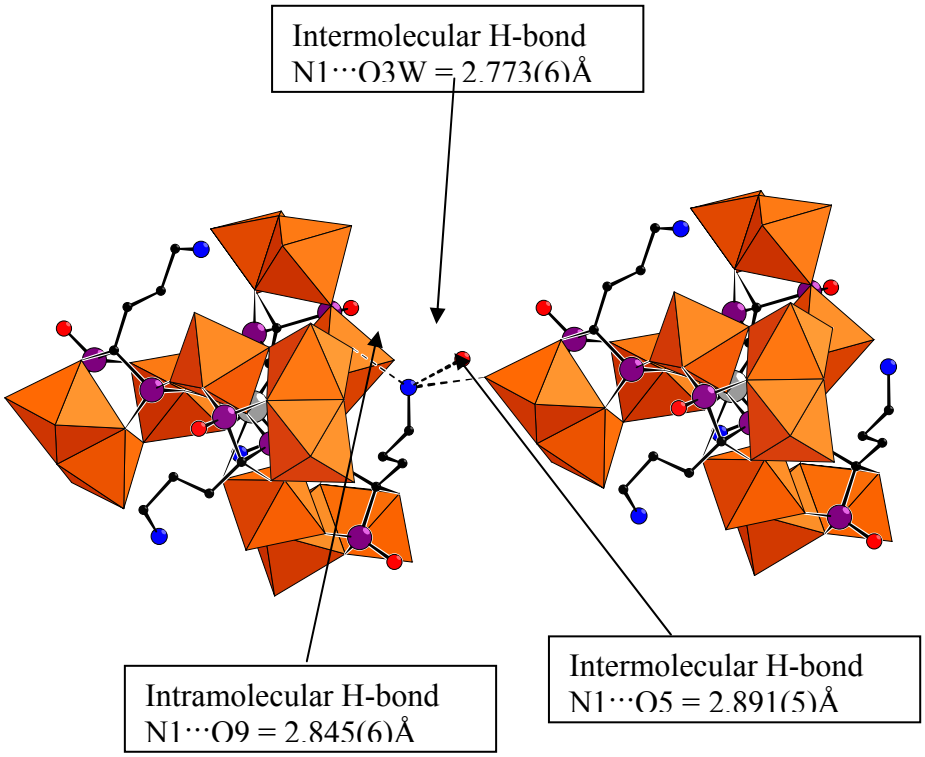

Fig . ESI2a : Details of the H-bond interactions between the nitrogen atom of the ligand and three surrounding oxygen atoms in **2** (the four nitrogen atoms of the POM are equivalent).

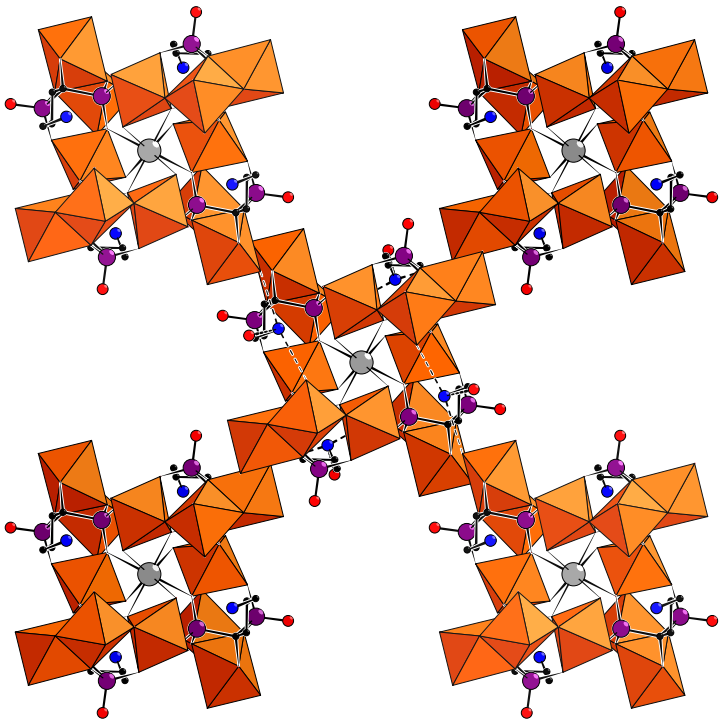

Fig . ESI2b : View of one POM and the four H-bonded neighbouring POMs in **2**.

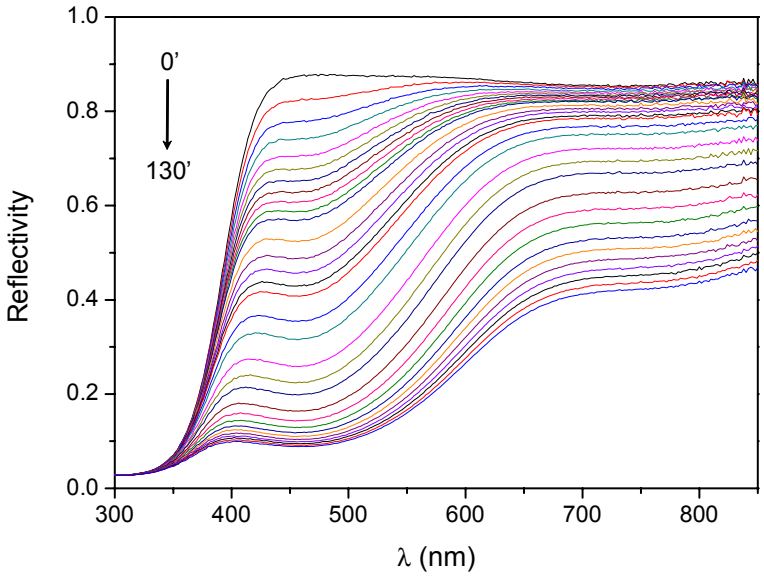

Fig. ESI3 : Reflectivity R(t) of **1** in the 300 – 850 nm range measured after irradiating the sample with UV light at 365 nm for 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, 10, 12.5, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 and 130 min.

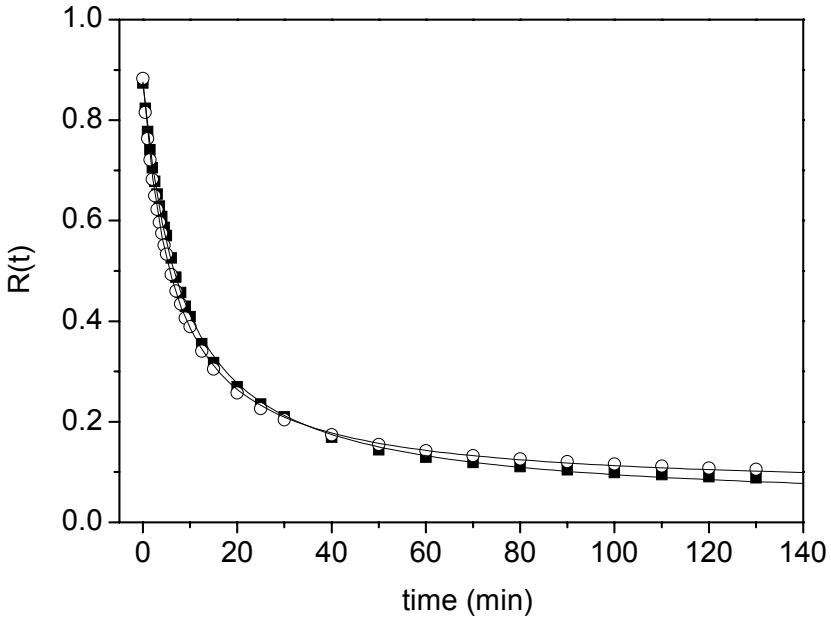

Fig. ESI4 : Reflectivity R(t) vs. t plots for (■) **1** and (○) **2** measured at 464 nm for 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, 10, 12.5, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 and 130 min of UV irradiation at 365 nm.

	1	**2**
$R^{464}(0)$	0.874	0.882
a	0.843	0.819
b	0.121	0.135
$R^{2(a)}$	0.99941	0.99963
$t_{1/2}$ (min)	8.264	7.407
k_i/k_1	1.000	1.148

Tab. ESI2 : Regression coefficient Values of the fitting parameters describing the R(t) vs t relationships for **1** and **2**.

The R(t) vs t relationships for **1** and **2** are perfectly fitted by $R^{464}(t) = a/[bt+1] + [R^{464}(0)-a]$. (see reference 4c for details of the kinetics model used here). $R^{464}(0)$ is the reflectivity value at t = 0, i.e., at the time just before UV illumination. The a parameter is the difference between the reflectivity values at t = 0 and at t = ∞, i.e. at the end of the photochromic process. The b parameter is defined as $b = k*C_{6+,r}(0)$, where k is the coloration rate constant, and $C_{6+,r}(0)$ is the concentration of photo-reducible Mo^{6+} centers in the materials. The half-life $t_{1/2}$, is defined as the time required for R(t) to reach the $[R(0)+R(\infty)]/2$ value. $t_{1/2}$ is given by $t_{1/2} = b^{-1}$. The k_i/k_1 (i = 1 – 2) ratios are the relative rate constants.

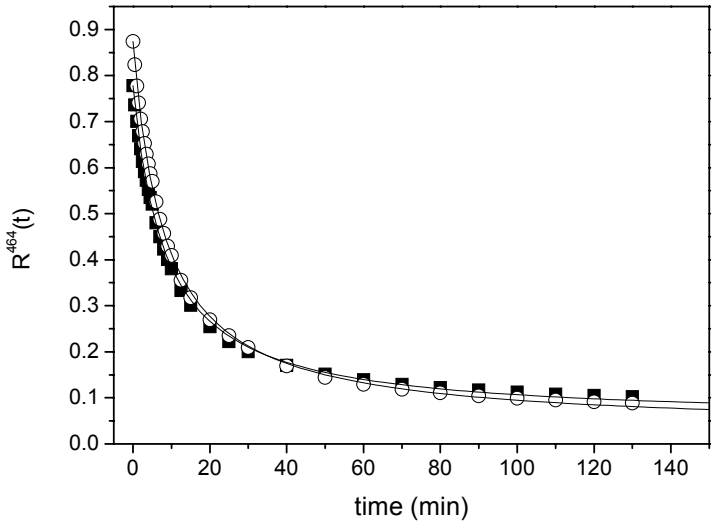

Fig. ESI5 : Reflectivity R(t) vs. t plots for (○) **1** and the deuterated analogue of **1** (■) **1-D** measured at 464 nm for 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, 10, 12.5, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 and 130 min of UV irradiation at 365 nm.

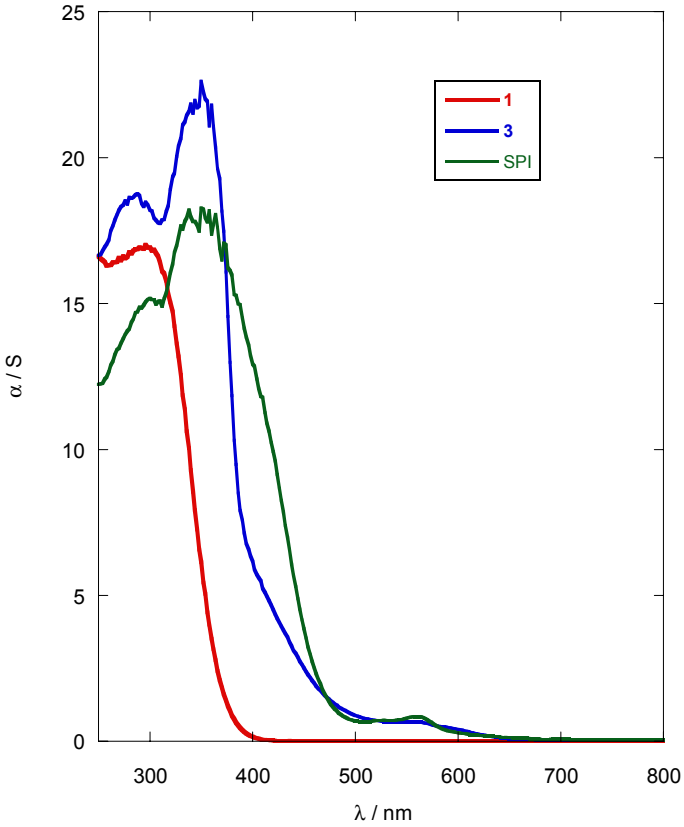

Fig. ESI6 : Kubelka-Munk transformed reflectivity of **1, 3** and SPI showing the absence of charge-transfer phenomenon in **3**.

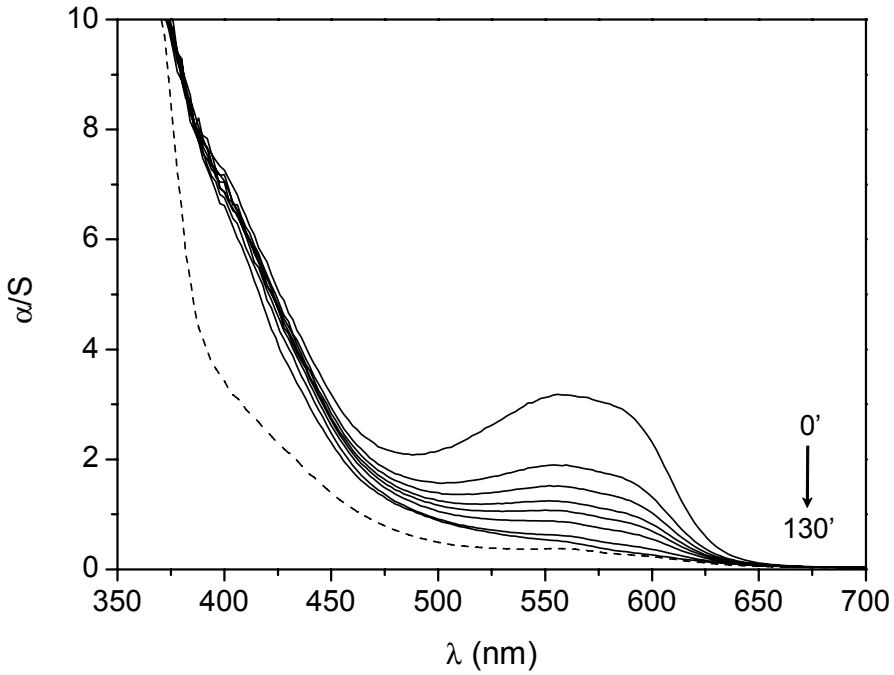

Fig. ESI7 : Kubelka-Munk transformed reflectivity of **3** irradiated at 365 nm for 30 min, at 0, 6, 10, 15, 20, 30, 70, and 130 min after cutting off the UV irradiation. The dashed line indicates the Kubelka-Munk transformed reflectivity of **3** before UV excitation. The yellowish-brown color of **3** reached in few minutes is deeper than its initial color before UV irradiation, showing that the absorption bands intensity decrease is faster for those related to the merocyanin form of the SP^+ cation than for the one devoted to the POM.