Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A single-crystal-to-single-crystal transformation affording photochromic 3D MO*R*F crystals

Xue Yang, Michel Giorgi, Hakim Karoui, Didier Gigmes, Virginie Hornebecq, Olivier Ouari, Anthony Kermagoret and David Bardelang

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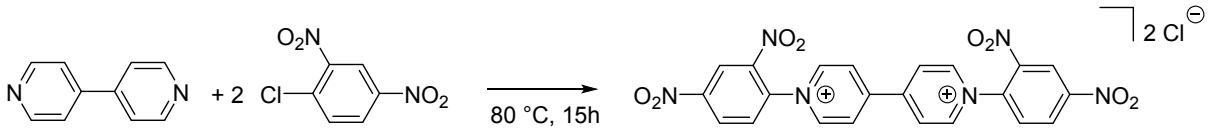
Experimental procedures

1/ Chemical compounds, NMR and UV reactor for photochromism. The chemicals: 4-4'-bipyridine, 1-chloro-2,4-dinitro-benzene, 4-amino-benzoic acid, $Zn(NO_3)_2.6H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, $Fe(Ac)_2$, 1-butyl-3-methylimidazolium chloride (**BMIC**), NaOH, HCl (35% in water), D_2O, DMSO-d_6, ethanol, acetone, EtOAc, DMF, DEF were purchased from commercial sources (Aldrich, Acros or TCI) and used without further purification. CB[7] was prepared according to a previous paper.[1] A Rayonet© photochemical reactor was used for the tests of photochromism with 15 light bulbs emitting at a wavelength of 305 nm. NMR spectra were acquired on BRUKER Avance III nanobay – 300 or 400 spectrometers (300.13 MHz and 400.13 MHz for ^{1}H NMR, and 75.46 MHz and 100.60 MHz for ^{13}C NMR respectively). D_2O was used as the solvent and a watergate sequence (water suppress) as well for ^{1}H NMR spectra (altering signals and integrals near 4.7 ppm). Acetone was also used as an internal reference (resonance set at 2.22 ppm).[2] Splitting patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet.

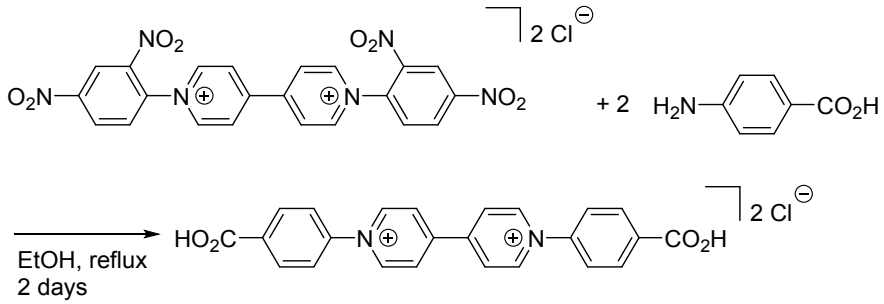
2/ Synthesis of PVP

Synthesis of 1,1'-bis(2,4-dinitrophenyl)-4,4'-Bipyridinium dichloride



To 0.90 g of bipyridine (5.8 mmol), was added 4.50 g of 1-chloro-2,4-dinitro-benzene (22.2 mmol) and the reaction was conducted in bulk at 80 °C for 15 h under magnetic stirring.
The resulting mixture was washed four times with 25 mL of hot ethanol and three times with acetone and dried under vacuum to yield a white powder. Yield: 2.05 g, 3.65 mmol, 63%.
^{1}H NMR (300 MHz, D_2O) δ 9.55 (d, *J* = 6.7 Hz, 4H, -N$^+$-C*H*), 9.49 (d, *J* = 2.2 Hz, 2H, NO_2C-C*H*-CNO_2), 9.01 – 8.83 (6H, overlapped of -N$^+$-CH-C*H (4H)* and NO_2C-C*H*-CH *(2H)*), 8.49 (d, *J* = 8.7 Hz, 2H, NO_2C-CH-C*H*). ^{1}H NMR spectra are in agreement with the literature.[3]
(Remark: the synthesis of 1,1'-bis(2,4-dinitrophenyl)-4,4'-Bipyridinium dichloride from bipyridine and 1-chloro-2,4-dinitro-benzene was performed at reflux in various solvents (MeOH, EtOH,[3] DMF or CH_3CN) but the best yield was obtained in bulk with 4 equiv. of 1-chloro-2,4-dinitro-benzene (melting point of 54 °C).

Synthesis of 4,4'-bis(carboxyphenyl)-bipyridinium dichloride



To a solution of 3.4 g of 1,1'-bis(2,4-dinitrophenyl)-4,4'-Bipyridinium dichloride (6.05 mmol) in 100 mL of ethanol was added 4.0 g of 4-amino-benzoic acid (29.2 mmol) and the reaction was conducted at reflux for two days. After reaction, a dark solid was filtered and a dark solution was removed. The dark solid was washed three times with ethanol (3*25 mL) and EtOAc (3*25 mL) and four times with DMF using a sonic bath (4*15 mL) to remove a dark solution, four times with acetone (4*25 mL) and dried under vacuum to yield a pale beige powder. Yield: 1.9 g, 4.05 mmol, 67%.
^{1}H NMR (300 MHz, DMSO) δ 13.98 – 13.26 (broad signal, 2H, CO_2H), 9.78 (br s, 4H, Ar), 9.15 (br s, 4H, Ar), 8.32 (d, *J* = 7.9 Hz, 4H, -N$^+$-C*H*-), 8.12 (d, *J* = 7.9 Hz, 4H, -N$^+$-CH-C*H*).

(Remark: even if 4,4'-bis(carboxyphenyl)-bipyridinium dichloride is not very soluble in DMSO, a ^{1}H NMR of the compound in DMSO-d_6 is required to ensure the absence of impurities which are not visible in D_2O).
^{1}H NMR (300 MHz, D_2O) δ 9.49 (d, *J* = 6.9 Hz, 4H, Ar), 8.86 (d, *J* = 6.9 Hz, 4H, Ar), 8.37 (d, *J* = 8.7 Hz, 4H, -N$^+$-C*H*-), 7.98 (d, *J* = 8.7 Hz, 4H, -N$^+$-CH-C*H*).
^{1}H NMR spectra are in agreement with the literature.[3]

3/ NMR measurements and K_a determination.

Following the ^{1}H NMR method of L. Isaacs and coll.,[4] Macartney and coll.[5] and D. Bardelang and coll.,[6] the binding constant between ***PVP*** and CB[7] was determined using 1-butyl-3-methylimidazolium chloride (**BMIC**) as a competitor.

Solutions of **BMIC** or **BMIC**@CB[7] and competitive solutions of **BMIC**, CB[7] and ***PVP*** (Eq 1 and Eq 2) were prepared (0.8mM, ratio **BMIC**/CB[7]/***PVP*** 1/1/1 in D_2O) before ^{1}H NMR test. According to the acquired ^{1}H NMR spectra, the values of the observed chemical shifts δ_{obs} of the CH_3-protons of the butyl group of free **BMIC** (δ_{obs_BMIC} = 0.90 ppm, Figure S1a) and **BMIC**@CB[7] ($\delta_{obs\_BMIC@CB[7]}$ = 0.09 ppm, Figure S1b) were determined. The chemical shift difference of CH_3-protons between free **BMIC** and **BMIC**@CB[7] was 0.81 ppm. The ^{1}H NMR spectra of competitive solutions of **BMIC**, CB[7] and ***PVP*** (Figure S1c) showed the values of the δ_{obs_CH3} (observed chemical shifts CH_3-protons of the butyl group in the competition) of **BMIC**. Values δ_{obs_CH3} were used to evaluate the concentrations of free **BMIC** and **BMIC**@CB[7] (fast exchange, Eq 3 and Eq 4), and so to calculate the concentration of free ***PVP*** and ***PVP***@CB[7] (Eq 5 and Eq 6), leading to the binding constant of ***PVP*** in the ***PVP***/CB[7]/**BMIC** equilibrium (ratio 1/1/1, 0.8 mM, Eq2).[6] Besides, the binding constant of **BMIC** of 151000 ± 5000 M^{-1} (obtained under the same conditions a in previous study)[6] was used for calculation of the binding constant K_a between ***PVP*** and CB[7] based on the relevant equilibrium.[6]

Eq 1 {BMIC ·CB[7]} + PVP ⇄ BMIC + {PVP·CB[7]}

Eq 2 $$K^{comp} = \frac{[BMIC] * [\{PVP•CB[7]\}]}{[\{BMIC•CB[7]\}] * [PVP]} = \frac{K^{1:1\ PVP}}{K^{1:1\ BMIC}} \Rightarrow \frac{[BMIC] * [\{PVP•CB[7]\}] * K^{1:1\ BMIC}}{[\{BMIC•CB[7]\}] * [PVP]} = K^{1:1\ PVP}$$

Eq 3 $$[BMIC] = \frac{(\delta_{obs\_CH3}) - (\delta_{obs\_BMIC•CB[7]})}{(\Delta\delta_{obs\_CH3})} * [BMIC]_{total} = \frac{(\delta_{obs\_CH3}) - 0.09}{0.81} * [BMIC]_{total}$$

Eq 4 $$[\{BMIC•CB[7]\}] = \frac{(\delta_{obs\_BMIC}) - (\delta_{obs\_CH3})}{(\Delta\delta_{obs\_CH3})} * [BMIC]_{total} = \frac{0.90 - (\delta_{obs\_CH3})}{0.81} * [BMIC]_{total}$$

Eq 5 [{***PVP***•CB[7]}] = $[CB[7]]_{total}$ - [{BMIC•CB[7]}] ($[CB[7]]_{free}$ is negligible).

Eq 6 [***PVP***] = $[***PVP***]_{total}$ - [{***PVP***•CB[7]}]

Table S1. Calculation of the binding constant of ***PVP*** toward CB[7] from ^{1}H NMR data.

Ratio of **BMIC**/CB[7]/***PVP***	$\delta_{obs\_CH3\ (average)}$[a]	% of free ***PVP***	Calculated binding constant of ***PVP***[b]
1/1/1	0.740 ppm	63	380000 ± 20000 M^{-1}

[a]chemical shift of C*H*$_3$-group of butyl of **BMIC** δ_{obs_CH3}, the presented value is the average of three NMR experiments, concentration of each species: 0.8 mM. [b]Standard deviation calculated based on three measurements.

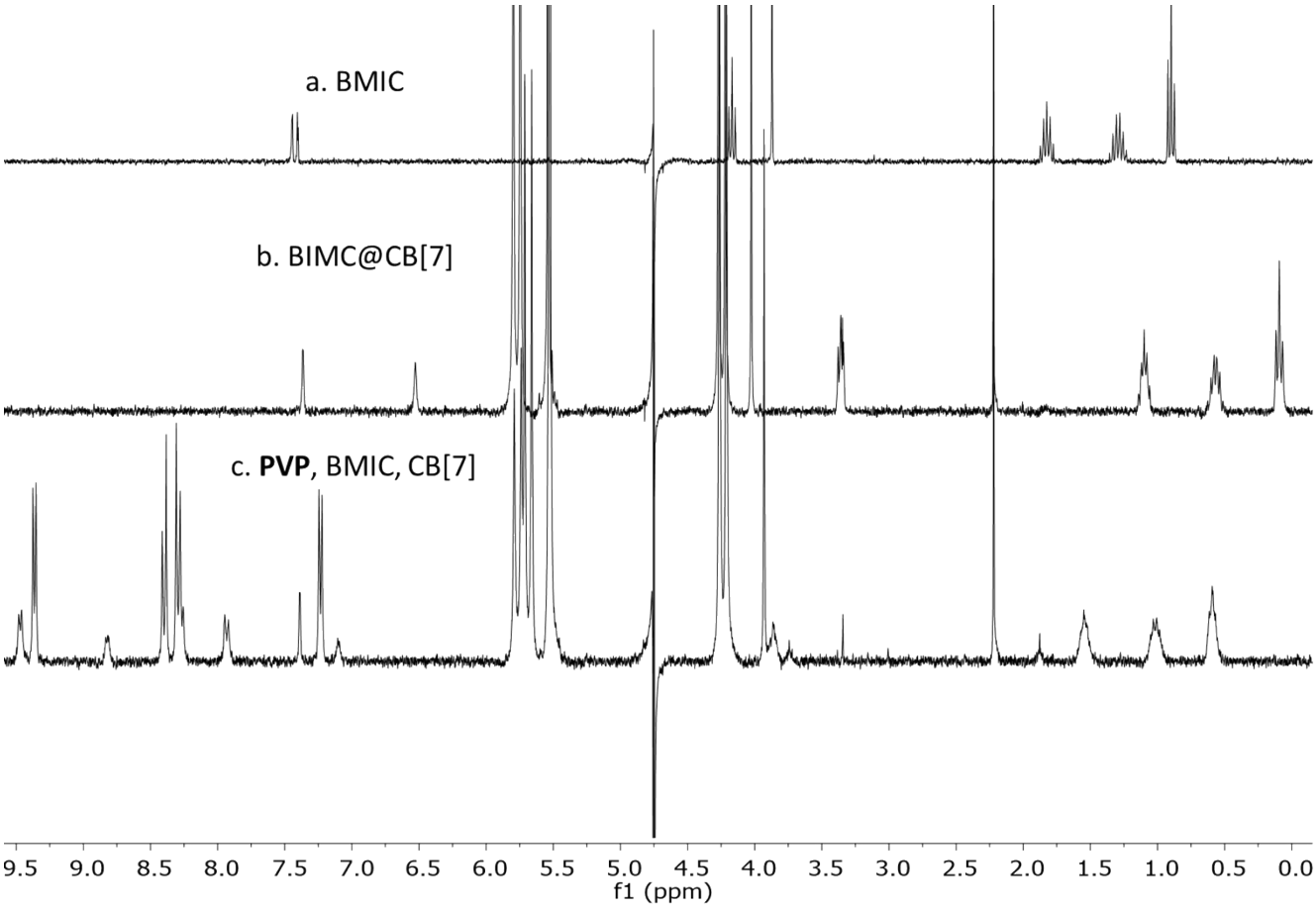


Figure S1. ^{1}H NMR spectra (watergate sequence) of **BMIC** (a), **BMIC**@CB[7] complex (b) and a mixture of **BMIC**, CB[7] and ***PVP*** (c, ratio 1/1/1, 0.8 mM each in D_2O). The spectra were calibrated using traces of acetone as internal reference (δ = 2.22 ppm).

4/ Screening of experimental conditions for crystal growth.
Chemicals were introduced in the following order in 20 cm height glass tubes: ***PVP***, CB[7],and water, before ultrasound to solubilize the complex. Then relevant metal salts followed by DMF (or DEF) were introduced in the tubes before sealing and heating them overnight.

Table S2. Screening conditions for experiments involving Zinc.

Name	$[M^+]$	[***PVP***]	[CB7]	V_{H2O}	V_{DMF}	V_{DEF}	conditions
PVP-01 Zn	175 mM / 208 mg	27 mM / 50 mg	28 mM / 131 mg	2 mL	2 mL	-	17H, 100°C, **NO**
PVP-02 Zn	128 mM / 76 mg	21 mM / 20 mg	24 mM / 55 mg	1 mL	1 mL	-	HCl, pH 5, 17H, 100°C, **NO**
PVP-03 Zn	128 mM / 76 mg	21 mM / 20 mg	24 mM / 55 mg	1 mL	1 mL	-	NaOH 1M, pH 10, 17H, 100°C, **NO**
PVP-04 Zn	80 mM / 95 mg	14 mM / 25 mg	15 mM / 68 mg	4 mL	-	-	17H, 100°C, **NO**
PVP-05 Zn	80 mM / 95 mg	14 mM / 25 mg	15 mM / 68 mg	2 mL	2 mL	-	17H, 100°C, yellow crystals, **suitable**
PVP-06 Zn	160 mM / 95 mg	27 mM / 25 mg	29 mM / 68 mg	1 mL	-	1 mL	17H, 100°C, yellow crystals, **suitable**
PVP-07 Zn	53 mM / 95 mg	9 mM / 25 mg	10 mM / 68 mg	2 mL	4 mL	-	17H, 100°C,
PVP-08 Zn	32 mM / 95 mg	5 mM / 25 mg	6 mM / 68 mg	2 mL	8 mL	-	17H, 100°C,
PVP-09 Zn	32 mM / 95 mg	5 mM / 25 mg	6 mM / 68 mg	8 mL	2 mL	-	17H, 100°C, YES, OK
PVP-10 Zn	32 mM / 95 mg	5 mM / 25 mg	6 mM / 68 mg	8 mL	2 mL		17H, 140°C, **NO**
PVP-11 Zn	32 mM / 95 mg	5 mM / 25 mg	6 mM / 68 mg	8 mL	2 mL		17H, 100°C, CB[7] batch with acid traces from *column*, **NO**
PVP-12 Zn	32 mM / 95 mg	5 mM / 25 mg	6 mM / 68 mg	7 mL	3 mL		17H, 100°C, YES, OK
PVP-13 Zn	32 mM / 95 mg	5 mM / 25 mg	6 mM / 68 mg	9 mL	1 mL		17H, 100°C, **NO**
PVP-14 Zn	32 mM / 95 mg	5 mM / 25 mg	6 mM / 68 mg	7 mL	3 mL		17H, 100°C, CB[7] batch with acid traces from *column*, **NO**
PVP-15 Zn	32 mM / 95 mg	5 mM / 25 mg	6 mM / 68 mg	9 mL	1 mL		17H, 100°C, CB[7] batch with acid traces from *column*, **NO**
PVP-16 Zn	64 mM / 95 mg	10 mM / 25 mg	12 mM / 68 mg	4 mL	1 mL		17H, 100°C, YES, OK
PVP-17 Zn	160 mM / 95 mg	25 mM / 25 mg	30 mM / 68 mg	1.6 mL	0.4 mL		17H, 100°C, YES, OK
PVP-18 Zn	40 mM / 95 mg	6.7 mM / 25 mg	7.3 mM / 68 mg	4 mL	4 mL	-	17H, 100°C, **NO**
PVP-19 Zn	20 mM / 47 mg	3.5 mM / 13 mg	3.7 mM / 34 mg	4 mL	4 mL	-	17H, 100°C, **NO**
PVP-20 Zn	10 mM / 24 mg	1.6 mM / 6 mg	1.8 mM / 17 mg	4 mL	4 mL	-	17H, 100°C, **NO**

***PVP*-21 Zn**	5 mM / 12 mg	0.8 mM / 3 mg	0.9 mM / 8 mg	4 mL	4 mL	-	17H, 100°C, **NO**

Table S3. Screening conditions for experiments involving Copper and Iron.

Name	[M^+]	[***PVP***]	[CB7]	V_{H2O}	V_{DMF}	V_{DEF}	conditions
***PVP*-22 Cu**	68 mM/ 95mg	9 mM / 25 mg	10 mM / 68 mg	2 mL	4 mL	-	17H, 100°C, small green crystals, unsuitable
***PVP*-23 Cu**	40mM/ 95mg	5 mM / 25 mg	6 mM / 68 mg	2 mL	8 mL	-	17H, 100°C, **NO**
***PVP*-24 Cu**	40mM/ 95mg	5 mM / 25 mg	6 mM / 68 mg	8 mL	2 mL	-	17H, 100°C, **NO**
***PVP*-25 Cu**	51mM/ 95mg	6.7 mM / 25 mg	7.3 mM / 68 mg	4 mL	4 mL	-	17H, 100°C, **NO**
***PVP*-26 Cu**	7.5mM/ 12mg	0.8 mM / 3 mg	0.9 mM / 8 mg	4 mL	4 mL	-	17H, 100°C, **NO**
***PVP*-27 Cu**	85 mM / 79 mg	14 mM / 25 mg	15 mM / 68 mg	4 mL	-	-	17H, 100°C, thin plates, unsuitable
***PVP*-28 Cu**	85 mM / 79 mg	14 mM / 25 mg	15 mM / 68 mg	2 mL	-	2 mL	17H, 100°C, **NO**
***PVP*-29 Fe**	85 mM / 59 mg	14 mM / 26 mg	15 mM / 70 mg	2 mL	2 mL	-	17H, 100°C, **NO**
***PVP*-30 Fe**	20 mM / 28 mg	3.5 mM / 13 mg	3.7 mM / 34 mg	4 mL	4 mL	-	17H, 100°C, **NO**
***PVP*-31 Fe**	20 mM / 28 mg	3.5 mM / 13 mg	3.7 mM / 34 mg	2 mL	6 mL	-	17H, 100°C, **NO**
***PVP*-32 Fe**	20 mM / 28 mg	3.5 mM / 13 mg	3.7 mM / 34 mg	1 mL	7 mL	-	17H, 100°C, small orange crystals, unsuitable
***PVP*-33 Fe**	24 mM / 34 mg	4.3 mM / 16 mg	4.5 mM / 41 mg	1 mL	7 mL	-	17H, 100°C, **NO**
***PVP*-34 Fe**	10 mM / 14 mg	1.75 mM / 6.5 mg	1.9 mM / 17 mg	1 mL	7 mL	-	17H, 100°C, **NO**
***PVP*-35 Fe**	15 mM / 21 mg	2.63 mM / 9.8 mg	2.8 mM / 26 mg	1 mL	7 mL	-	17H, 100°C, **NO**
***PVP*-36 Fe**	20 mM / 28 mg	3.5 mM / 13 mg	3.7 mM / 34 mg	1.5 mL	6.5 mL	-	17H, 100°C, small orange crystals, unsuitable
***PVP*-37 Fe**	22 mM / 31 mg	3.5 mM / 13 mg	3.7 mM / 34 mg	0.5 mL	7.5 mL	-	17H, 100°C, **NO**
***PVP*-38 Fe**	32 mM / 56 mg	5 mM / 25 mg	6 mM / 68 mg	8 mL	2 mL	-	17H, 100°C, **NO**
***PVP*-39 Fe**	64 mM / 112 mg	10 mM / 50 mg	12 mM / 136 mg	1.5 mL	6.5 mL	-	17H, 100°C, **NO**
***PVP*-40 Fe**	20 mM / 28 mg	3.5 mM / 13 mg	3.7 mM / 34 mg	1.5 mL	6.5 mL	-	17H, 100°C, **NO**
***PVP*-41 Fe**	144 mM	25 mM	26 mM	1.5 mL	6.5 mL		17H, 100°C, **NO**

Samples corresponding to conditions ***PVP*-09**, ***PVP*-12**, ***PVP*-16**, and ***PVP*-17**, afforded crystalline precursors of the 3D-MO*R*F crystals as checked by measurements of the unit cells of randomly collected crystals. When repeating the crystal growth, we noted that conditions corresponding to ***PVP*-09** and ***PVP*-12** afforded samples for which crystal growth took more time. More concentrated samples (***PVP*-16** and

PVP-17) allowed accelerating crystal growth and suitable crystals for single crystal XRD could be obtained within 2 to 5 days after cooling to room temperature.

***5/ Single crystal X-ray diffraction*.**
Suitable crystals for compounds Zn•***P-V-P***•CB[7]_125K and Zn•***P-V-P***•CB[7]_293K were measured on a Rigaku Oxford Diffraction SuperNova diffractometer at 125K and 293K respectively, at the CuKα radiation (λ=1.54184 Å). Data collection reduction and multiscan ABSPACK correction were performed with CrysAlisPro (Rigaku Oxford Diffraction). Using Olex2[7] the structures were solved by direct methods with SHELXT[8] and SHELXL[9] was used for full matrix least squares refinement. A mask of solvent[7] was applied to Zn•***P-V-P***•CB[7]_125K and the H-atoms were introduced manually at geometrical positions. All H-atoms for Zn•***P-V-P***•CB[7]_293K were found experimentally. For both compounds the coordinates and Uiso parameters for the H-atoms were constraint to 1.5Ueq(parent atoms) for the water molecules and to 1.2Ueq(parent atom) for the CH and CH_2.

The phase transition from Zn•***P-V-P***•CB[7]_125K to Zn•***P-V-P***•CB[7]_293K was obtained by keeping the crystal on the diffractometer after the measurement at 125K and rising the temperature to room temperature while blowing the sample overnight with dry air.

Compound	Zn.*P-V-P*.CB[7]_125K	Zn.*P-V-P*.CB[7]_293K
Formula	$C_{66}H_{75.2}N_{31}O_{29.6}Zn_{0.5}$	$C_{33}H_{29}N_{15.5}O_{10.5}Zn_{0.25}$
M_w	1809.05	827.06
Crystal system	orthorhombic	tetragonal
Temp./ K	125	293
Space group	F dd2	I -4 2 d
a/ Å	46.597(3)	32.6797(2)
c/ Å	14.9947(15)	13.5625(2)
V/ Å^3	32173(6)	14484.2(3)
Z	16	16
Dc/g.cm^{-3}	1.494	1.517
Crystal colour	yellow	green
Crystal size/mm^3	0.06*0.08*0.34	0.06*0.08*0.34
μ(Mo-Kα)/mm^{-1}	1.168	1.152
N° of refl. measured	30628	32827
N° of unique refl.	12698	6829
N° of obs. refl.[$F^2 > 4\sigma F^2$]	9301	6301
N° parameters refined	1181	544
R_1 [$F^2>4\sigma F^2$]	0.1272	0.0507
wR_1 [$F^2>4\sigma F^2$]	0.3584	0.1429
R_2 [all refl.]	0.1469	0.0547
wR_2 [all refl.]	0.3893	0.1476
Goodness of fit [all refl.]	1.359	1.091
Residual Fourier/e. Å^{-3}	-0.742; 0.789	-0.229; 0.593

***6/Thermogravimetric analysis*.** Measurements were carried out with a TGA Q500 apparatus (TA Instruments). The air flow was maintained during the whole experiment (12 hours) at a constant value of 40 ml/min and the temperature was fixed to T= 298 K.

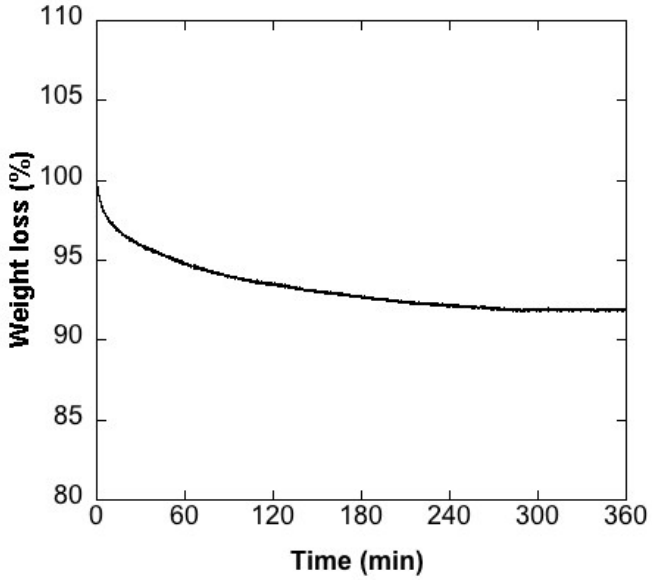


Figure S2. Isothermal thermogram (T=298 K) of low-temperature form crystals.

***7/ Powder X-ray diffraction*.** Powder X-Ray Diffraction pattern (PXRD) was recorded using a Siemens D500R diffractometer using Cu Kα radiation in the 6-20 ° 2θ range with a 0.01 ° step associated with a step time of 4 s. Prior to measurement, MO*R*F crystals were gently grounded to obtain a powder.

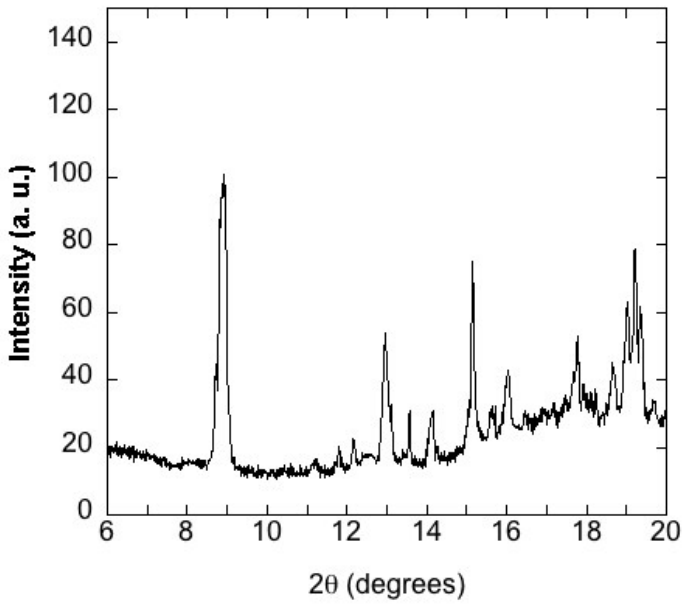


Figure S3. PXRD of MO*R*F crystals. There is a good agreement with the theoretical pattern extracted from the single crystal structure of the corresponding 3D-MO*R*F (dry phase).

***8/ Solid state UV-vis spectroscopy*.** UV-vis spectra on solids materials were recorded using a Varian Cary 300 spectrometer equipped with an integrating sphere DRA-CA-30I. Reported spectra are obtained by subtraction of the support from the solid spectra. Irradiation of yellow crystals was performed using a 150 W Xe lamp (Lot Oriel) as the UV source, for 2 minutes.

***9/ EPR measurements*.** Solid samples of the 3D-MO*R*F crystals (1.0 mg) were introduced in an EPR quartz tube before irradiation for 2 minutes in the Rayonet© photochemical reactor at 305 nm. EPR measurements were performed right after the irradiation by introducing the tube as quickly as possible in a Bruker Elexsys E500 spectrometer operating at 9.4 GHz (X-band). The following parameters were used: microwave power 20 mW, receiver gain 99, time constant 0.128 s, sweep width 120 to 200 G, sweep time 30 s, modulation amplitude of 1 G and 5 scans. We noticed a rather rapid signal loss with time (second timescale). The transition is reversible and the crystals can be photoactivated again reversibly.

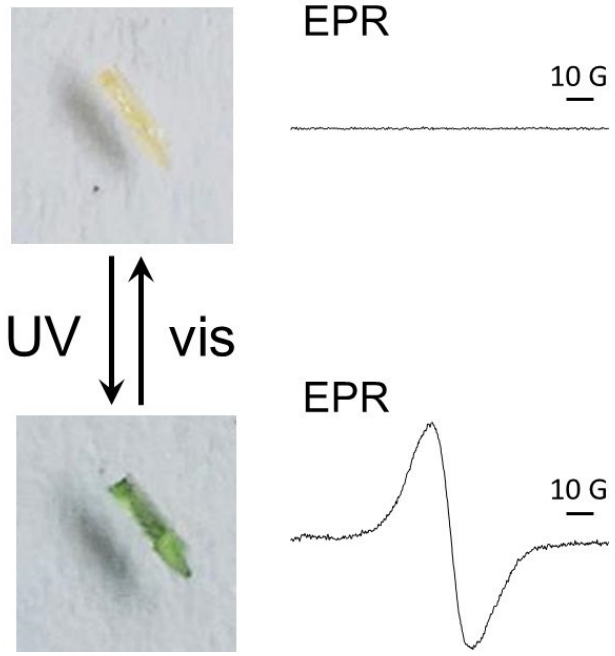


Figure S4. EPR spectra of the 3D-MO*R*F Zn•***P-V-P***•CB[7] crystals at room temperature, before (top) and after (bottom) irradiation with UV light.

10/ References.

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