Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Neutral Mo_6Q_8-clusters with terminal phosphine ligands – a route to water soluble molecular units of Chevrel phases

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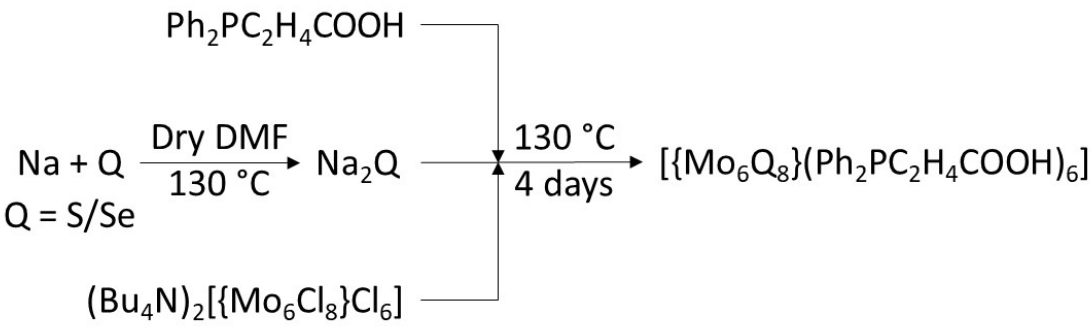

Figure S1. The schematic illustration of the synthesis of **1** and **2**.

Table S1. List of solubility of **1** and **2** in common solvents.

Solvent	1	2	sodium salt of 1	sodium salt of 2
DMF	+	+	-	-
DMSO	+	+	-	-
Acetone	-	-	-	-
Acetonitrile	-	-	-	-
Ethanol	+	+	-	-
Diethyl ether	-	-	-	-
Water	-	-	+	+

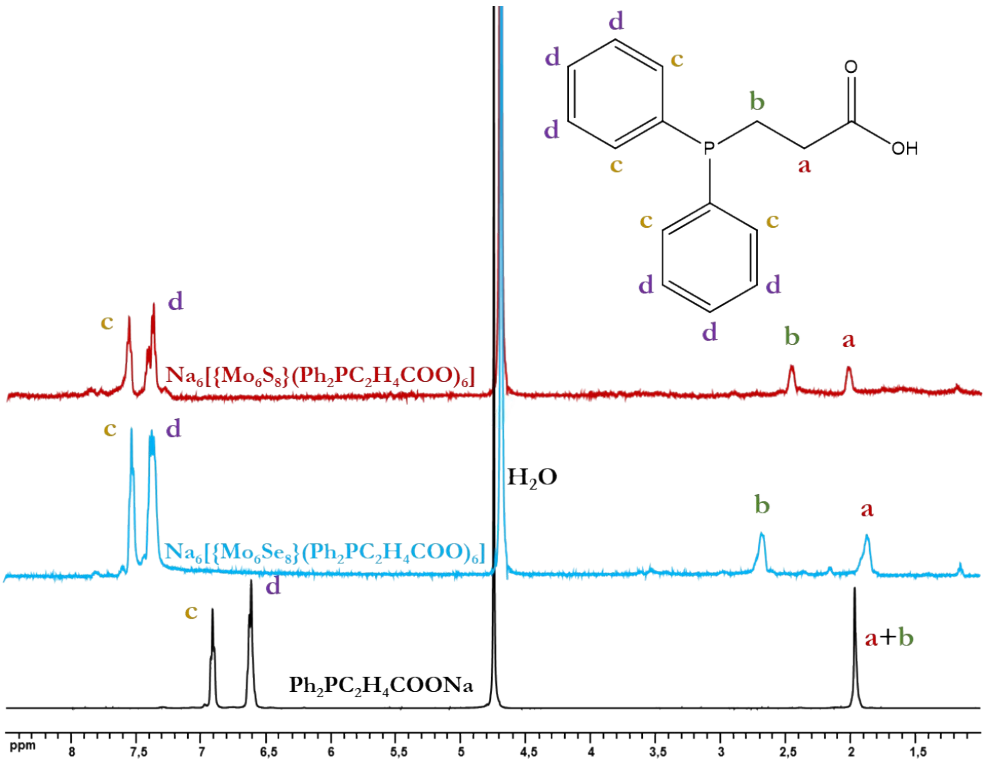

Figure S2. ^{1}H NMR spectra of $Ph_2PC_2H_4COOH$ and sodium salts of **1** and **2**.

Table S2. Selected crystallographic parameters of the single-crystal X-ray diffraction structural analysis for **1** and **2**

Parameter	**1**·4.5H_2O·2.5Et_2O	**2**·4.5H_2O·2.5Et_2O
Empirical formula	$C_{100}H_{124}Mo_6O_{19}P_6S_8$	$C_{100}H_{124}Mo_6O_{19}P_6Se_8$
Formula weight	2647.92	3023.12
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
Z	1	1
T (K)	150(2)	150(2)
a (Å)	14.2549(6)	14.3781(9)
b (Å)	15.2377(5)	15.2185(9)
c (Å)	17.0827(7)	17.2172(10)
α (°)	98.206(2)	97.527(2)
β (°)	108.992(2)	109.711(2)
γ (°)	114.838(1)	114.890(2)
V (Å)	3010.5(2)	3048.4(3)
D_{calc} (g cm^{-3})	1.461	1.647
μ (mm^{-1})	0.882	3.122
Crystal size (mm)	0.1 × 0.08 × 0.03	0.09 × 0.09 × 0.05
ϑ scan range (º)	1.973 to 30.595	2.278 to 25.737
Indices ranges	$-20 \le h \le 20$ $-21 \le k \le 21$ $-23 \le l \le 23$	$-17 \le h \le 17$ $-18 \le k \le 18$ $-20 \le l \le 20$
Reflections collected	60018	47618
Independent reflections	17241	11614
Observed reflections [I > 2σ(I)]	11944	6738
Parameters refined	748	746
R_{int}	0.0450	0.1048
Goodness-of-fit (GOF) on F^2	1.027	0.948
R_1^a/wR_2^b [I > 2σ(I)]	0.0460/0.1277	0.0551/0.1328
R_1^a/wR_2^b (all data)	0.0757/0.1408	0.1159/0.1539
$\Delta\rho_{max}/\Delta\rho_{min}$ (ē·$Å^{-3}$)	1.345/–0.988	1.179/–1.936

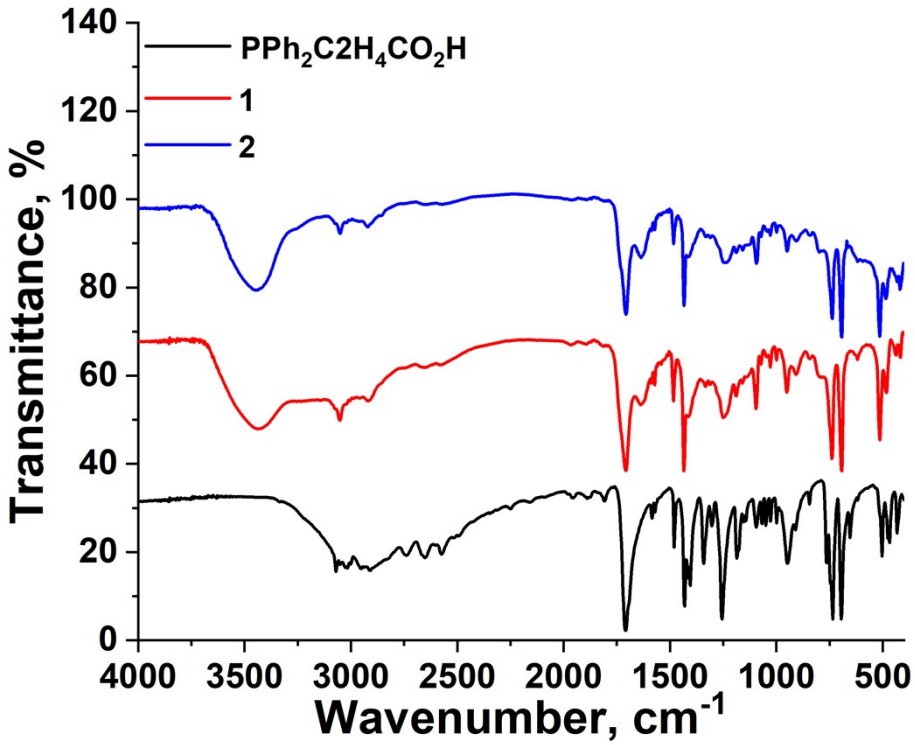

Figure S3. FTIR spectra of the pro-ligand and compounds **1** and **2**.

Table S3. Main intracluster distances in **1** and **2** and related compounds

Compound	Mo–Mo, Å	Mo–Q, Å	Mo–P, Å
1·4.5H_2O·2.5Et_2O	2.6540(4) – 2.6668(4)	2.4306(8) – 2.4648(8)	2.5444(9) – 2.5594(8)
2·4.5H_2O·2.5Et_2O	2.6947(10) – 2.7049(9)	2.531(1) – 2.574(1)	2.544(2) – 2.560(2)
[{Mo_6S_8}$(PEt_3)_6$][1]	2.662 – 2.664	2.438 – 2.449	2.527
[{Mo_6S_8}$(PEt_3)_6$][2]	2.658 – 2.666	2.445 – 2.463	2.525 – 2.537
[{Mo_6Se_8}$(PEt_3)_6$][3]	2.700 – 2.708	2.555 – 2.566	2.537 – 2.548

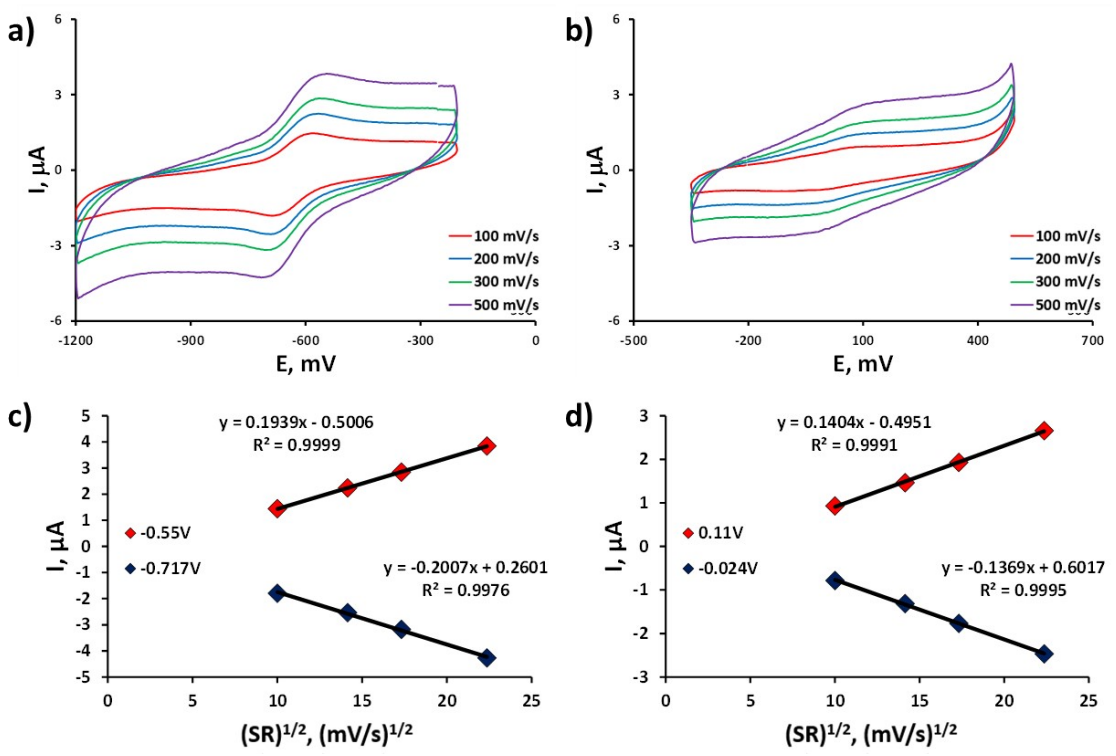

Figure S4. Cyclic voltammograms of **1** at various scan rate (a, b) and linear dependence of the anodic and cathodic peak current upon square root of the potential scan rate (c, d).

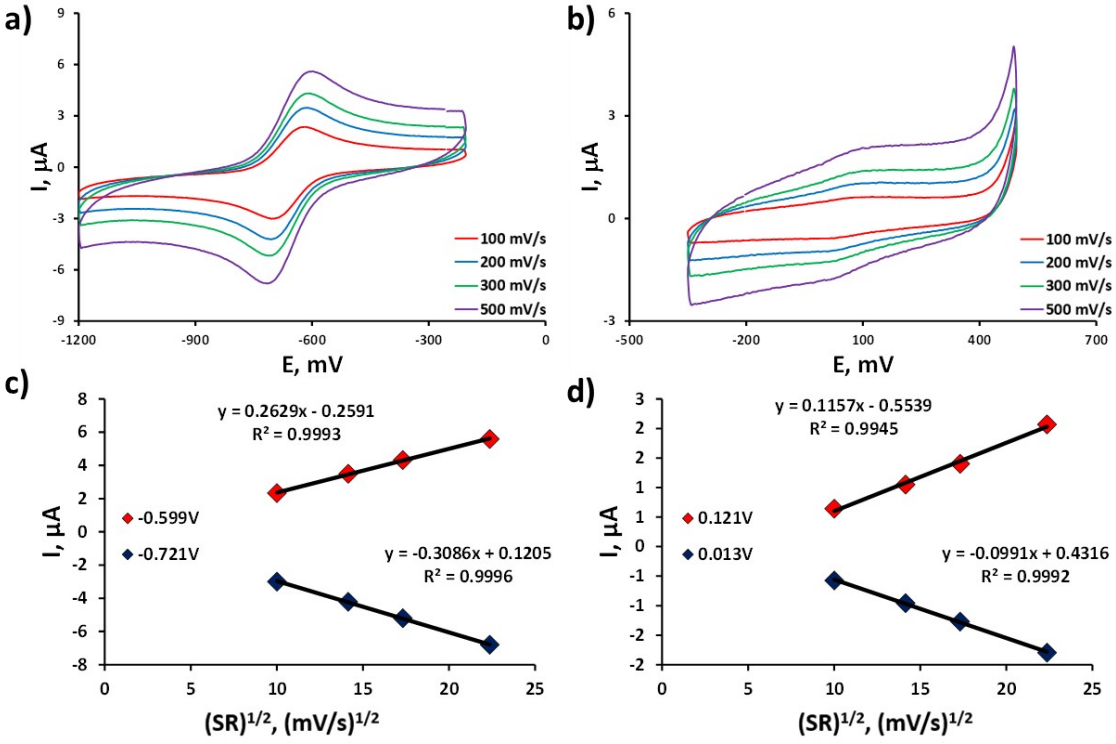

Figure S5. Cyclic voltammograms of **2** at various scan rate (a, b) and linear dependence of the anodic and cathodic peak current upon square root of the potential scan rate (c, d).

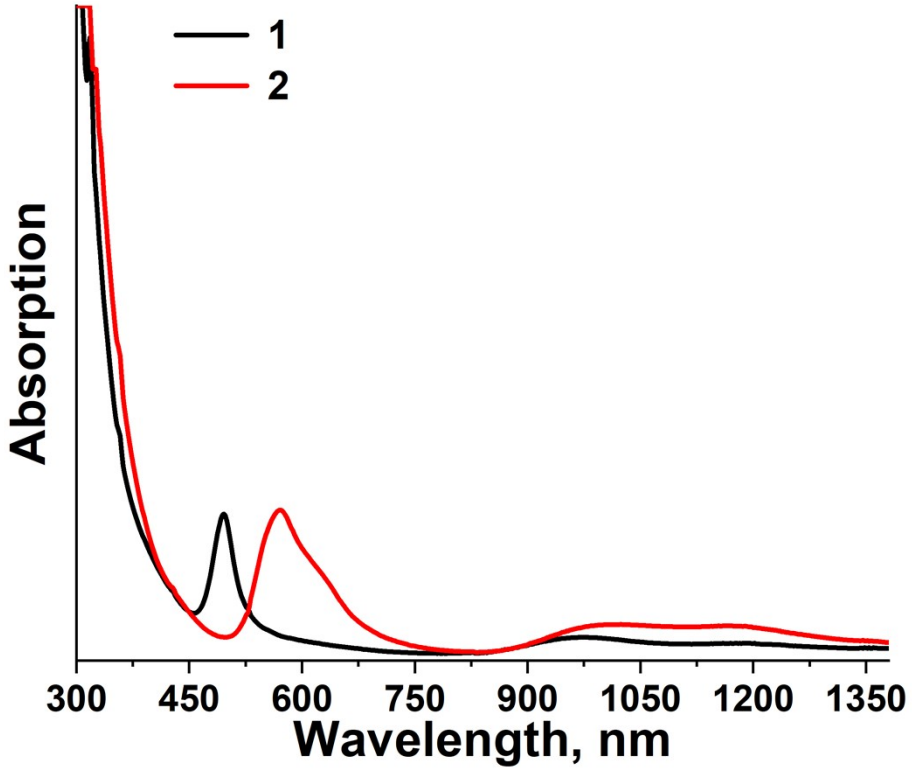

Figure S6. Absorption spectra of **1** and **2** in DMF.

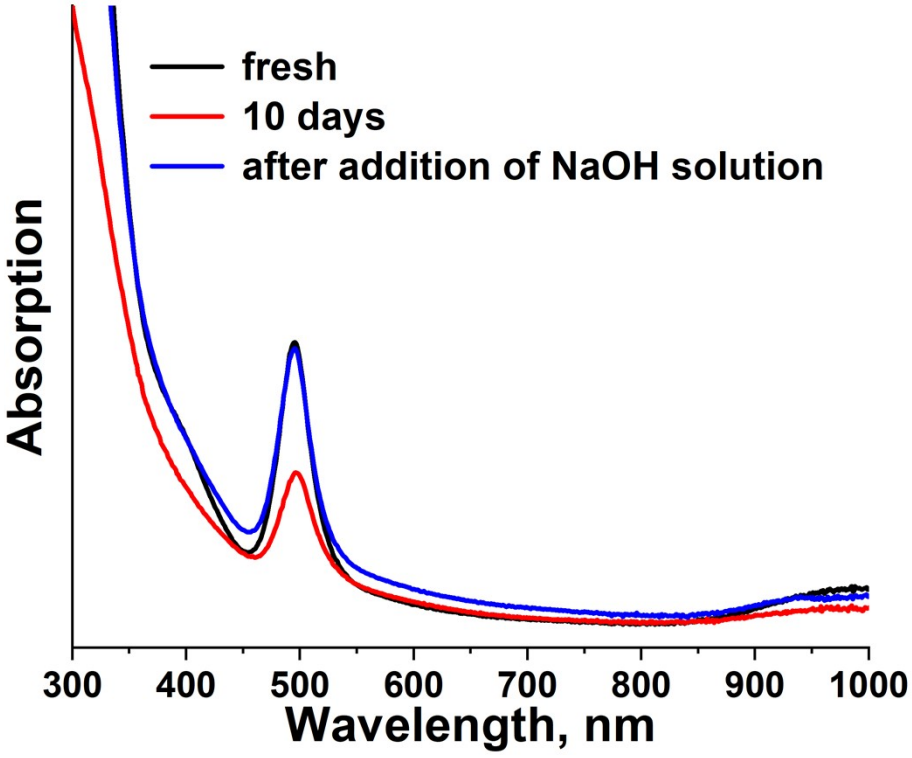

Figure S7. Absorption spectra of sodium salt of **1** in water: fresh (black), aged for 10 days (red), and after addition of NaOH solution (blue).

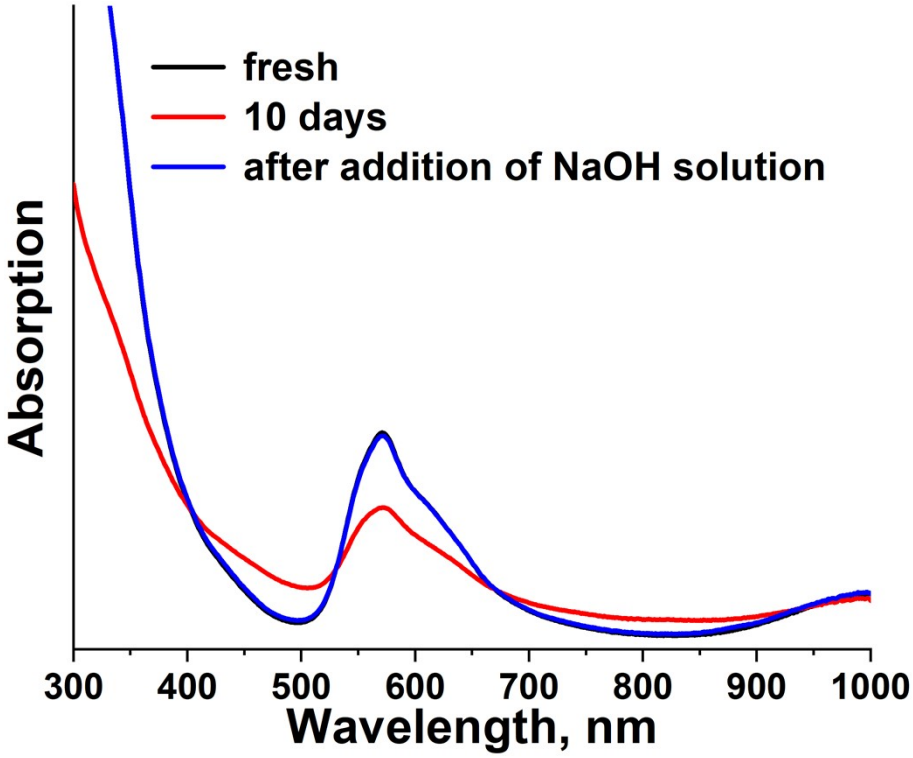

Figure S8. Absorption spectra of sodium salt of **2** in water: fresh (black), aged for 10 days (red), and after addition of NaOH solution (blue).

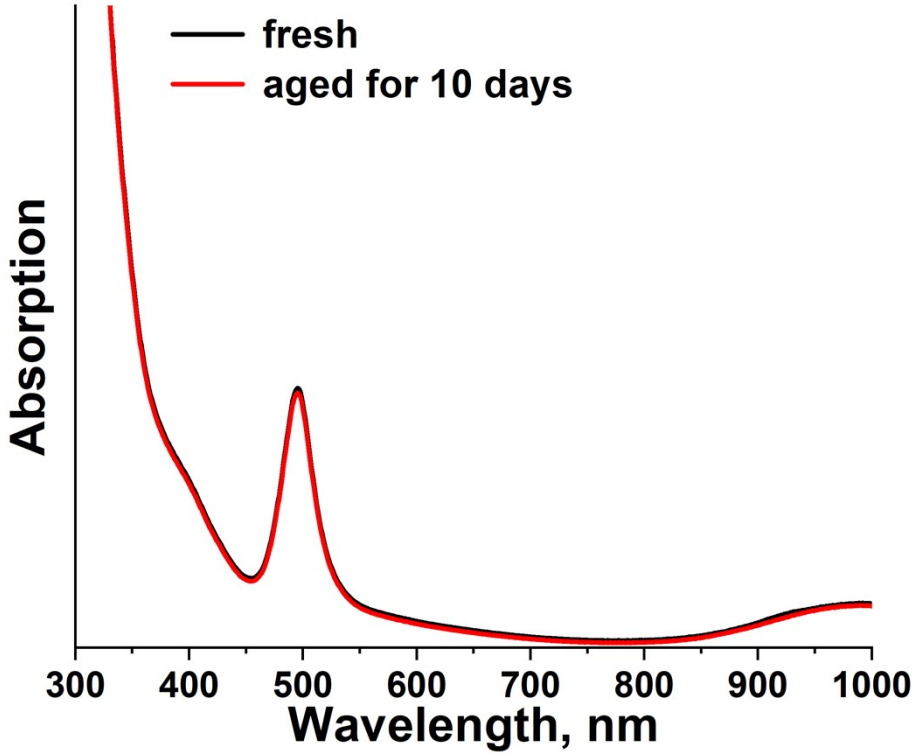

Figure S9. Absorption spectra of sodium salt of **1** in water aged for 10 days at pH ~ 13.

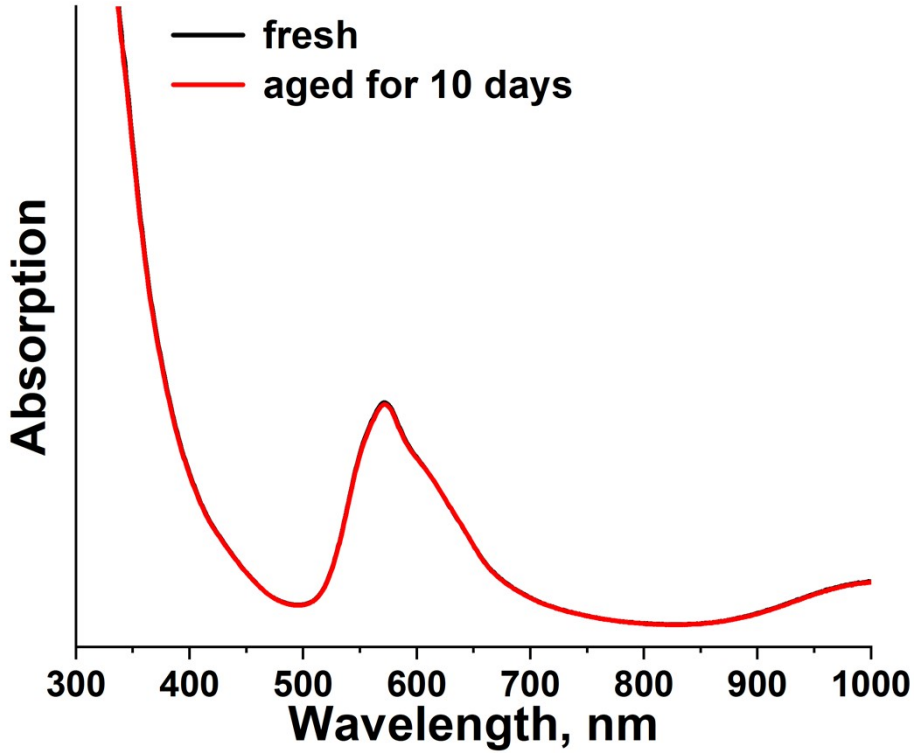

Figure S10. Absorption spectra of sodium salt of **2** in water aged for 10 days at pH ~ 13.

References

1. T. Saito, N. Yamamoto, T. Yamagata and H. Imoto, *J. Am. Chem. Soc.*, 1988, **110**, 1646-1647. https://doi.org/10.1021/ja00213a060
2. T. Matsumoto, R. Namiki and H.-C. Chang, *Eur J Inorg Chem*, 2018, **2018**, 3900-3904. https://doi.org/10.1002/ejic.201800587
3. T. Saito, N. Yamamoto, T. Nagase, T. Tsuboi, K. Kobayashi, T. Yamagata, H. Imoto and K. Unoura, *Inorg. Chem.*, 1990, **29**, 764-770. https://doi.org/10.1021/ic00329a039