Electronic Supplementary Information for Dalton Transactions

Supplementary Material

The First Porous MOF with Photoswitchable Linker Molecules

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(1) Synthesis of 3-azo-phenyl-4,4´-bipyridine

The synthesis of 3-azo-phenyl-4,4´-bipyridinewas accomplished in a 5 step synthesis procedure. All reaction steps, except the last one were carried out according to the literature (references [1] to [4]).

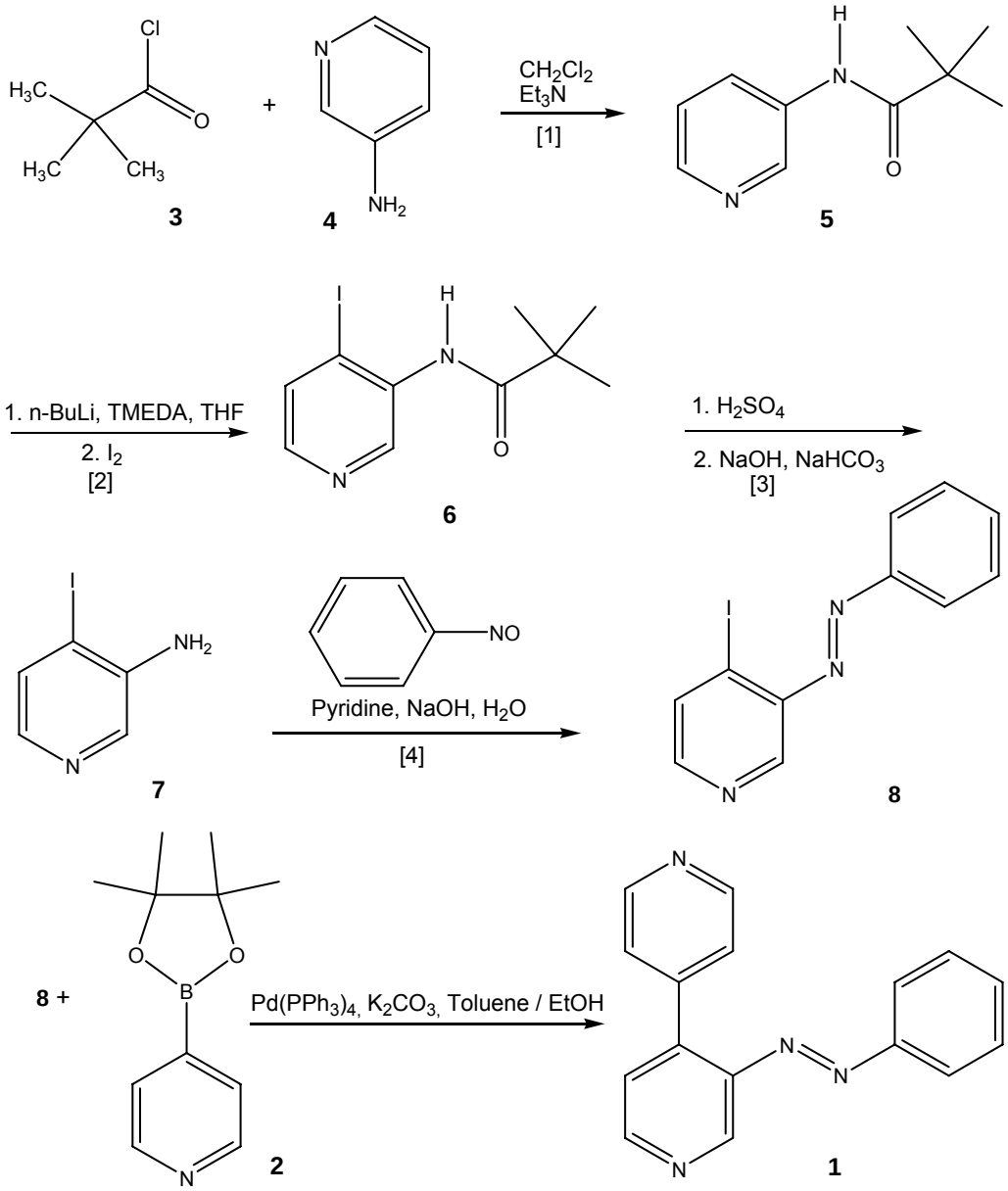

Figure S1. Five-step synthesis of the switchable azobipyridine linker molecule (1). The first four reaction steps were performed according to the literature.

[1] J. A. Turner, *J. Org. Chem.* **1983**, *43*, 3401.

[2] L. Estel, F. Marsais, G. Quéguiner, *J. Org. Chem.* **1988**, *53*, 2740.

[3] J. Malm, B. Rehn, A.-B. Hörnfeldt, S. Gronowitz, *J. Heterocyclic Chem.* **1994**, *31*, 11.

[4] C. Bornholdt, *Ph. D. Thesis*, Christian-Albrechts-Universität zu Kiel, **2008**.

(2) Results of the TG/DTA investigation of CAU-5

Figure S2 shows the results of the TG/DTA experiment. A total weight loss of 80.6 % is observed between 390 and 510°C. This is due to the decomposition of the network. The final product was identified as ZnO by PXRD and the calculated weight loss (80.1 %) corresponds well with the measured one.

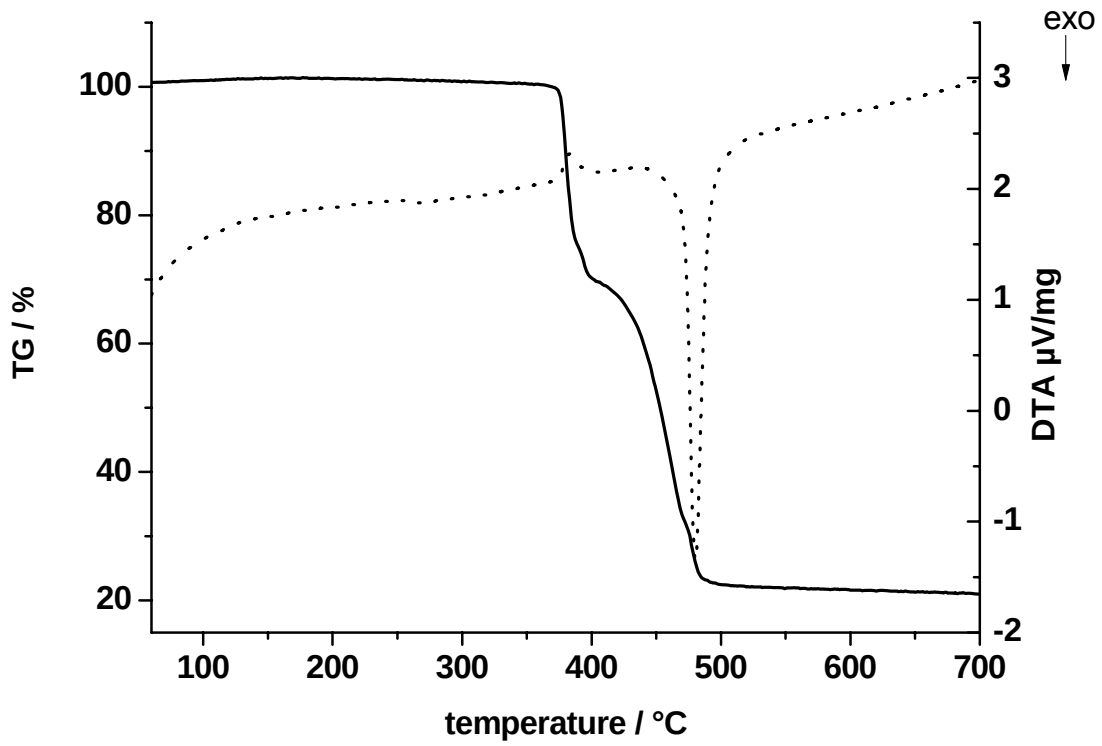

Fig. S2. TG and DTA curve of the thermal decomposition of CAU-5.

(3) UV/Vis spectrum of CAU-5

Figure S3 shows the results of the UV/Vis switching experimenst of CAU-5 microcrystals in a $BaSO_4$ matrix. After an irradiation period of 5 min with UV light (λ = 365 nm) the blue UV/Vis spectrum was recorded. Another 5 min of irradiation with the same wavelength led to the green UV/Vis spectrum. The red UV/Vis spectrum was recorded after an irradiation period of 15 min. This experiment shows, that after an irradiation period of 15 min with UV light (λ = 365 nm), the UV/Vis spectrum of CAU-5 in $BaSO_4$ does not show any further changes. Therefore, 15 min of irradiation was chosen for all switching experiments.

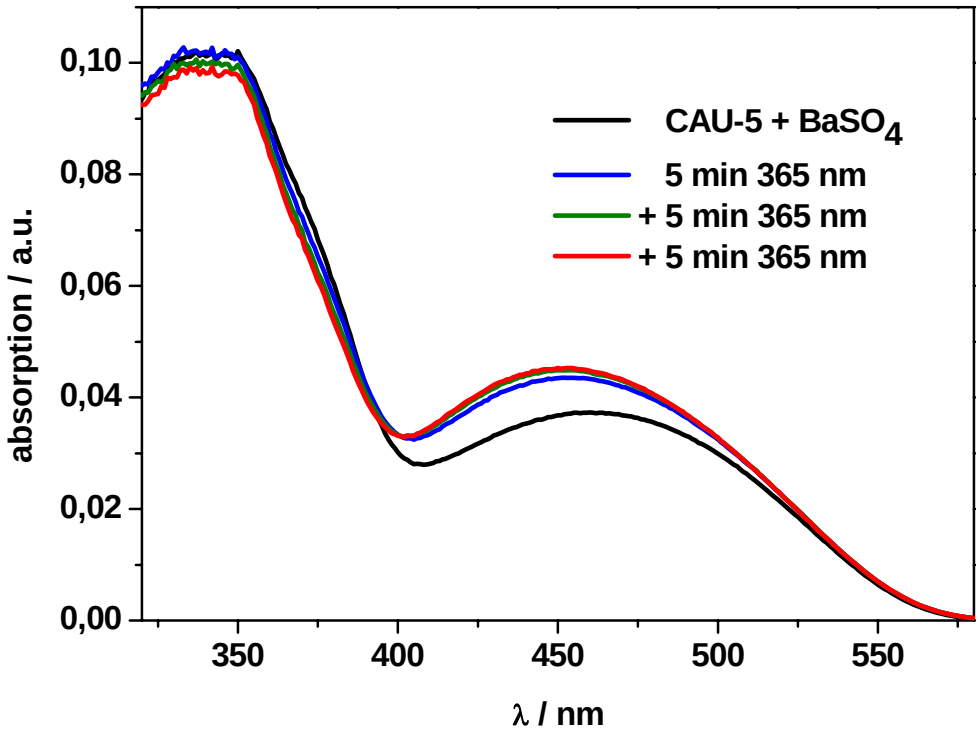

Fig. S3: UV/Vis spectrum of CAU-5 in $BaSO_4$: after an irradiation period of 15 min no further change is visible.

(4) XRPD patterns of the synthesis products obtained from the variation of the molar ratio of 3-azo-phenyl-4,4´-bipyridine : 4,4´-bipyridine

Figure S4 shows the XRPD patterns of the reaction products from the stepwise replacement of 4,4'-bipyridine by **1**. The comparison of the measurements of the mixed ligand systems with the theoretical powder pattern of $Zn_2(NDC)_2$4,4'Bipy (bottom) shows no changes in the reflection positions. The use of pure **1** leads to the new compound CAU-5 (top).

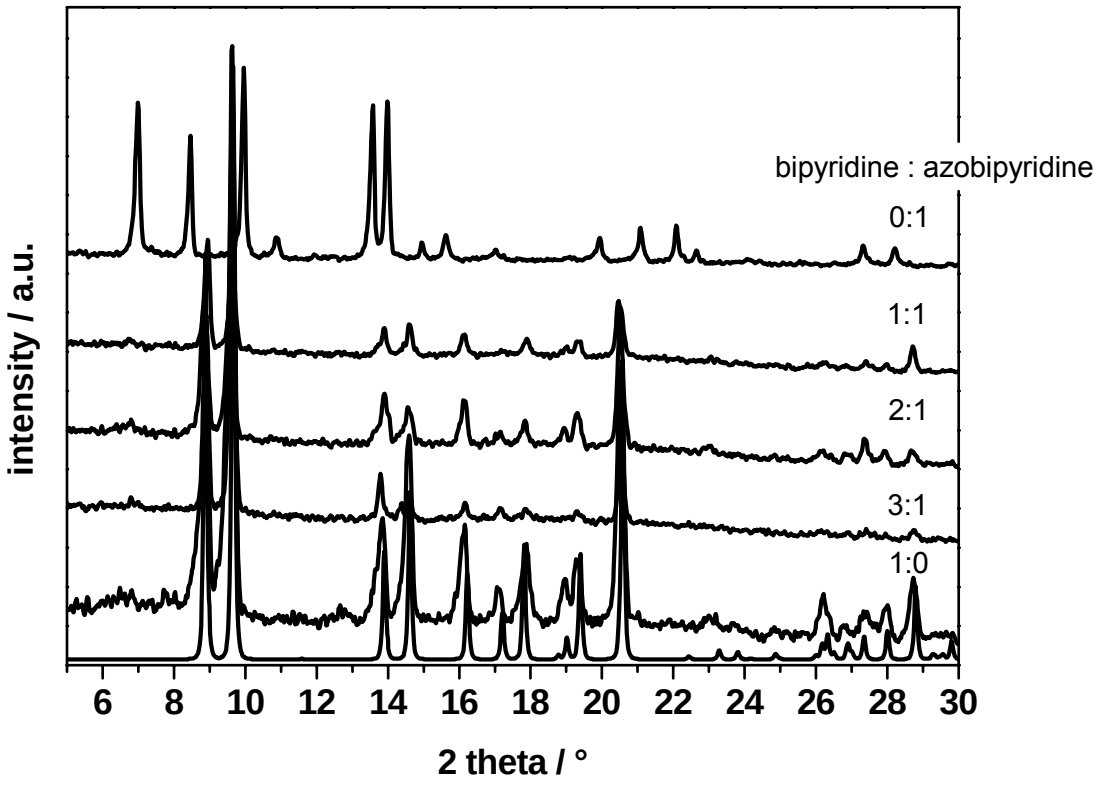

Fig. S4: XRPD pattern of the reaction products obtained by the stepwise replacement of 4,4'-bipyridine by 1. Bottom: theoretical powder pattern of [$Zn_2(NDC)_2$(4,4'-Bipy)].

(5) Raman-spectra of 3-azo-phenyl-4,4´-bipyridine, naphthalenedicarboxylic acid and CAU-5

The comparison of the Raman spectra of pure 3-azo-phenyl-4,4´-bipyridine (**1**), H_2NDC and CAU-5 are shown in Fig. S4. Wavenumbers of the bands are listed in Tab. S1. The characteristic *trans* -N=N- stretching vibration at 1444 cm^{-1} (marked by an asterisk) is present in both spectra. Almost all peaks observed in the spectra of H_2NDC and 3-azo-phenyl-4,4´-bipyridine are also visible in the Raman spectra of CAU-5.

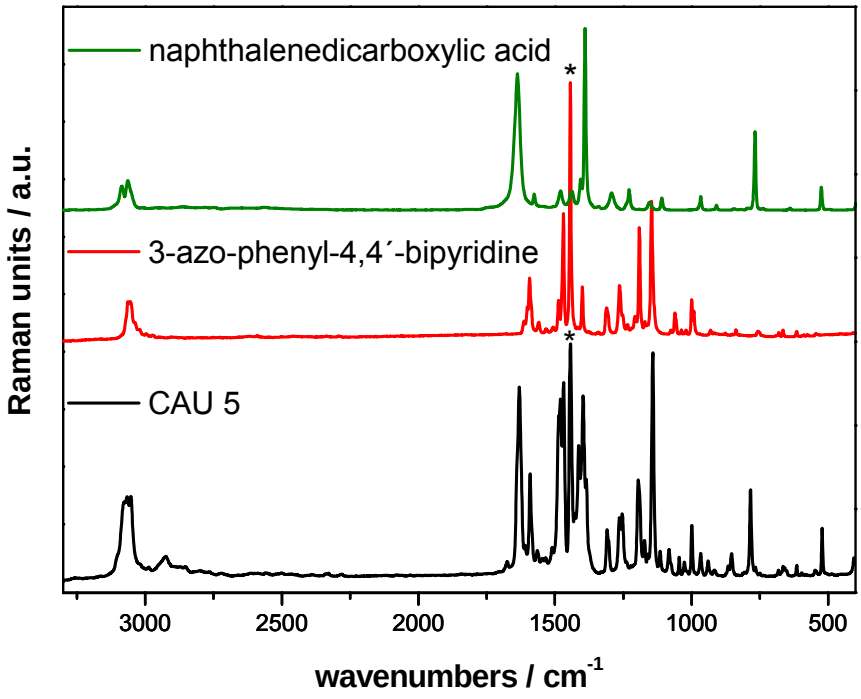

Fig. S5. Raman spectra of napthalenedicarboxilic acid, 3-azo-phenyl-4,4´-bipyridine and CAU-5.

Tab. S1: Assigment of Raman-signals.

1	NDC	CAU 5	assigment
	1636	1631	C=C str. vibration
1594	1577	1591	C=C str. vibration
1485	1479	1481	s-m, C=C, C=N in plane vib. or C-H sym. def. vibr.
1469		1469	s-m, C=C, C=N in plane vib. or C-H sym. def. vibr.
1443		1444	trans N=N vibration
		1427	s-m, C=C, C=N in plane vib.
	1407	1413	s-m, C=C, C=N in plane vib.
1398	1390	1397	aromt. ring vibration
		1385	aromt. ring vibration
1261		1265	arom. C-H in plane def.
1252		1254	arom. C-H in plane def.
1199		1196	arom. C-H in plane def.
		1173	arom. C-H in plane. def. vibr.
1142		1142	arom. C-H in plane def. vibr.
	1109	1115	arom. C-H in plane. def. vibr.
		1083	C=C str. vibr.
		1044	C-O str. vibr. or arom. C-H in plane. def. vibr.
		1025	arom. C-H in plane def. vibr.
998		999	s-m, C=C, C=N in plane vib. or arom. C-H in plane. def. vibr.
	966	966	out-of-plane def. vibr. (3 neigh. H)
		938	out-of-plane def. vibr. (1 isolated H)
		854	Naphthalene rings out-of plane vibr.
	529	522	out of plane def. vibr.

(6) CO_2 adsorption isotherm of CAU-5

Figure S6 shows the CO_2 adsorption isotherm of CAU-5 at 298 K. The maximum uptake of CO_2 at this temperature and 100 kPa is 50 cm^3/g.

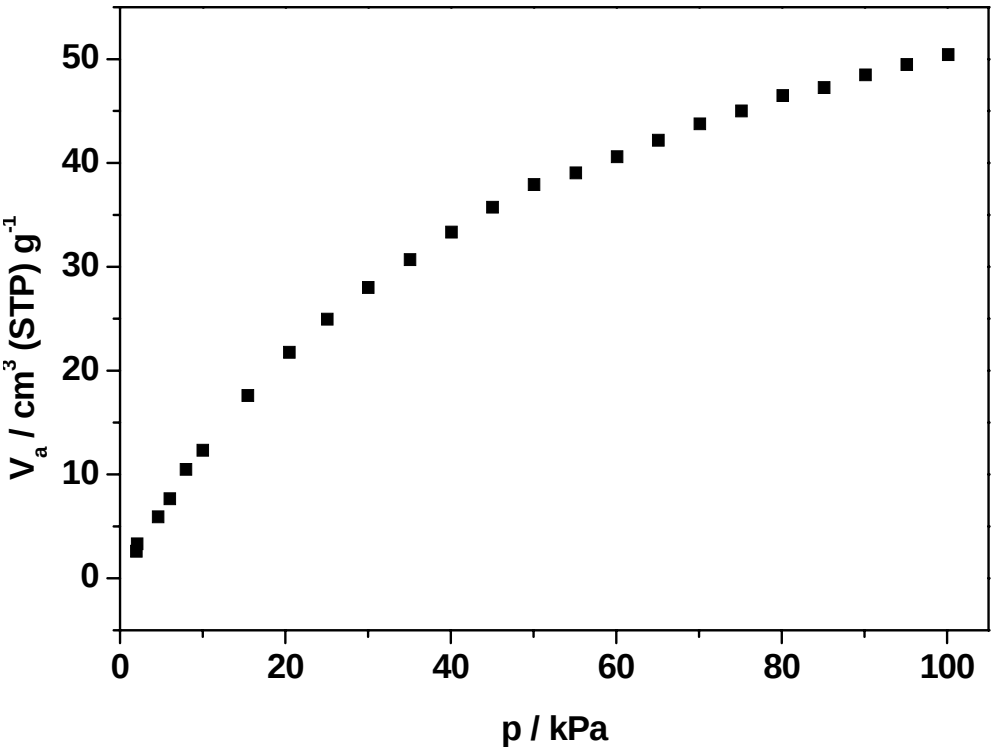

Fig. S6: CO_2 adsorption isotherm of CAU-5 measured at 298 K.

(7) Ar adsorption isotherm of CAU-5

Figure S7 shows the Ar-adsorption isotherm of CAU-5 at 77 K. Evaluation of the data with the Brunauer-Emmett-Teller (BET) equation results in a specific surface area of 805 m²/g.

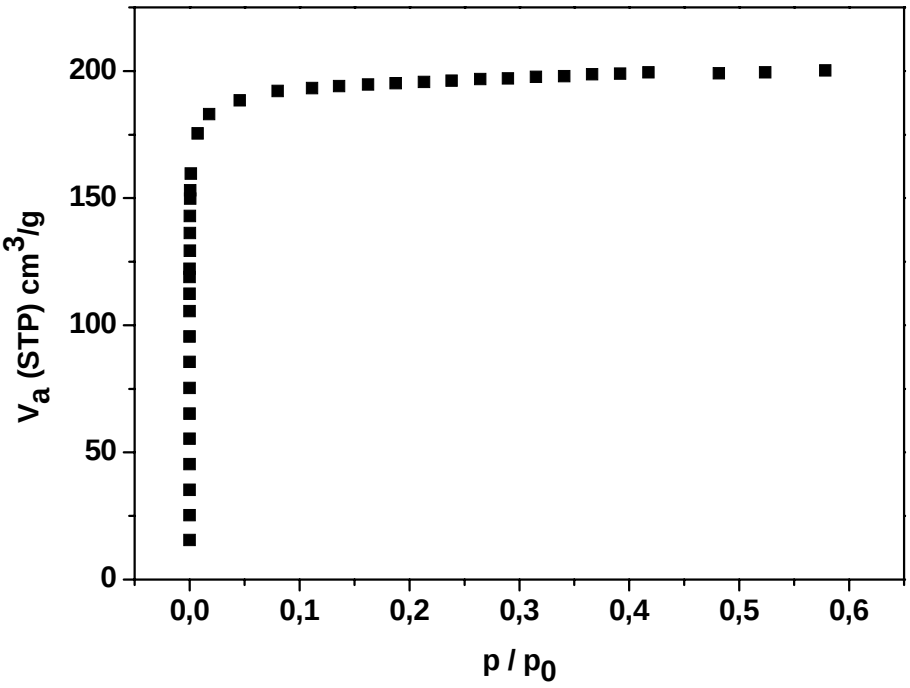

Fig. S7: Ar adsorption isotherm of CAU-5 measured at 77 K.

(8) Complete UV/Vis-spectrum of CAU-5 in a $BaSO_4$ matrix

Figure S8 shows the complete UV/Vis Spectrum from 320 to 600 nm of CAU-5 in a $BaSO_4$ matrix. After an irradiation time of 15 min with UV light (λ = 365 nm) (blue, gray, purple curve) the π → π* maximum decreased and the n → π* maximum increased due to higher *cis*-isomer concentration. After an irradiation time of 15 min with visible light (λ = 440 nm) (orange, red, green curve) the π → π* maximum increased again and the n → π* maximum decreased due to lower *cis*-isomer concentration.

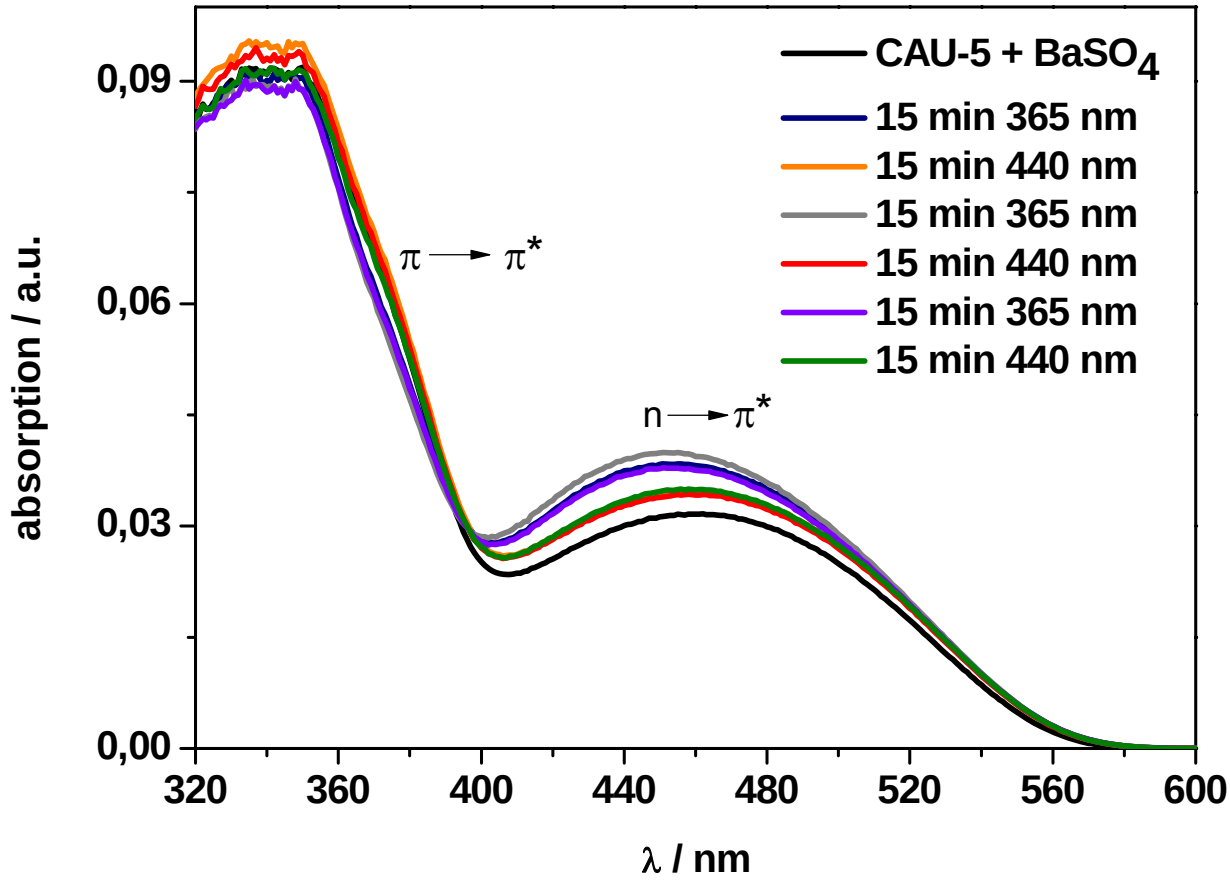

Fig. S8: UV/Vis spectrum of CAU-5: investigation of the switching behavior.

(9) Results of the multiple switching experiment of CAU-5

Figure S9 shows the absorption intensity at the maximum at 460 nm after the switching cycles (0.5 corresponds to the as synthesized material, cycles 1, 2, and 3 to switching with λ = 365 nm, and cycles 1,5, 2.5, and 3.5 to switching with λ = 440 nm). For fully reversible switching an ideal zig-zag curve should be observed.

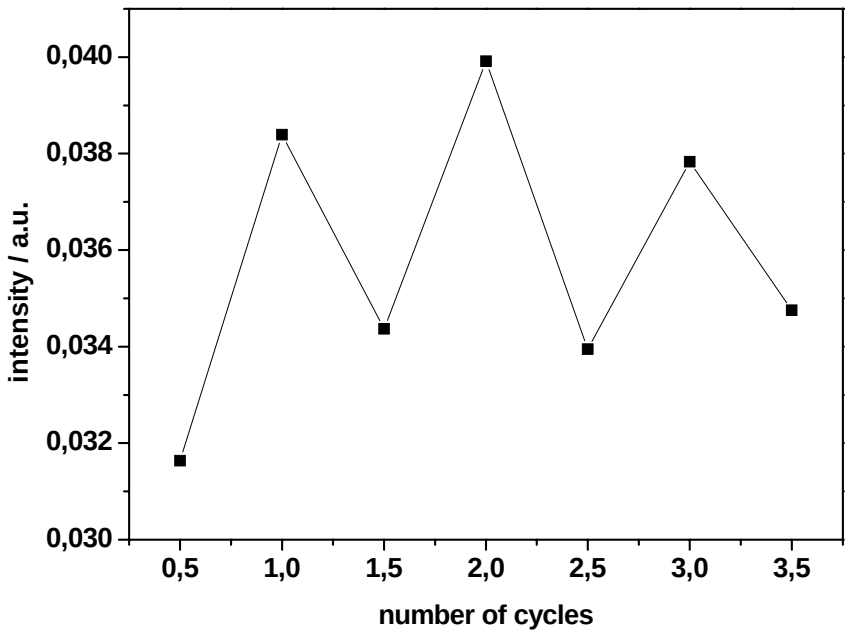

Fig. S9: Switching behavior of CAU-5 in $BaSO_4$.

(10) UV/Vis-spectrum of CAU-5, thermal relaxation

Figure S9 shows the UV/Vis spectra of CAU-5 in a $BaSO_4$ matrix. After an irradiation time of 15 min with UV light (λ = 365 nm) (green curve) the sample was left at room temperature in the dark for 24 h. After 24 h the red UV/Vis spectrum was recorded. The intensity at 460 nm decreased, but did not reach the original value at this point.

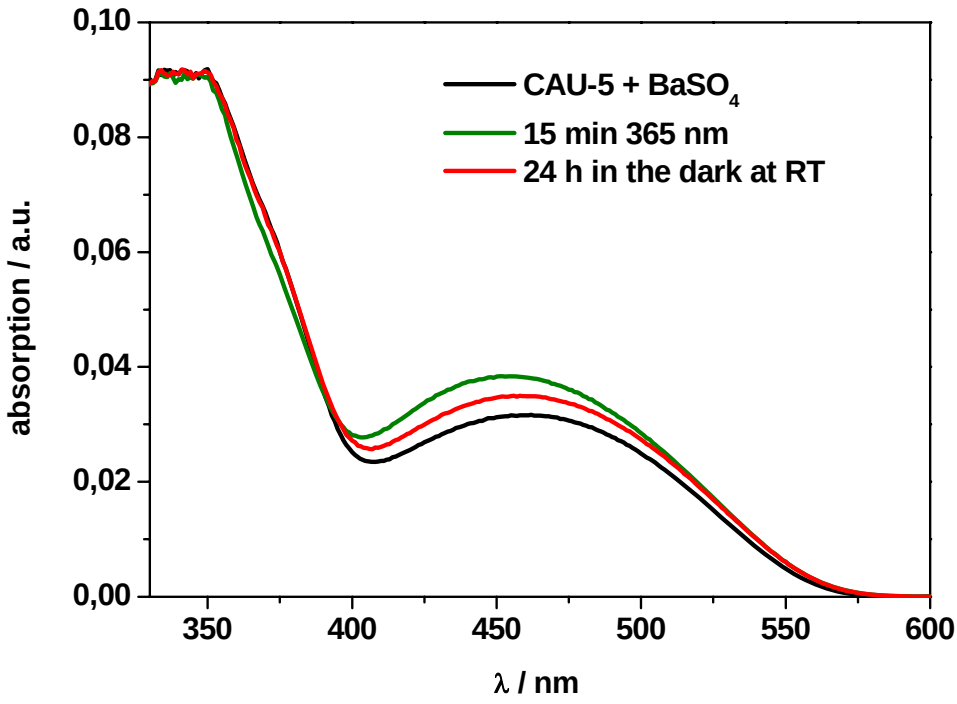

Fig. S10: UV/Vis spectrum of CAU-5: investigation of the thermal relaxation.