Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Multi-Stimuli Responsive Poly(azodibenzo-18-crown-6-ether)s

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Synthesis and Fractionation

The preparation of the starting monomers, the 4',4''- and 4',5''- dinitrodibenzo-18-crown-6-ethers (Fig. S1) occurs in the same reaction mixture. The 4',4''- product precipitates first from the medium and has a higher melting temperature (m_p=236°C), the 4',5''- counterpart (m_p=206°C) precipitates slowly overnight.

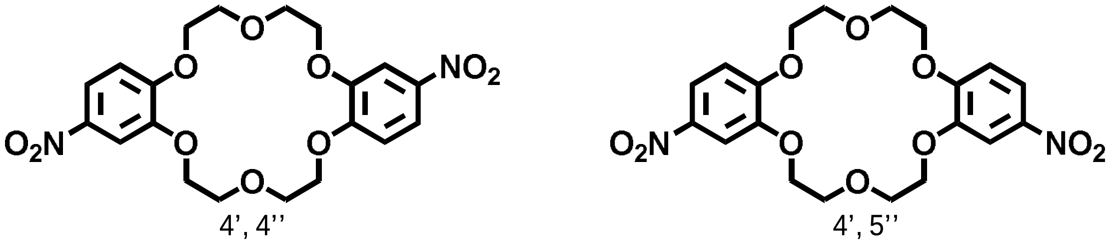

Fig. S1. Structure of monomers, 4',4''- and 4',5''-dinitrodibenzo-18-crown-6-ethers.

The mononitrodibenzo-18-crown-6-ether, was prepared under milder nitration conditions in good yield (Fig. S2) and was then used in the synthesis of a azobis(dibenzo-18-crown-6-ether) model compound, MC (Fig. S14). The reductive coupling used for the preparation of the main chain azo-polymers relies on the same procedure we have reported earlier[17]. By adjusting the ratio of sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) to monomer, reaction temperature and concentration (Fig. S3) we can induce the azo-bridge formation and thus the polymerization. However, this being a step-growth process, the crude reaction mixtures after SEC analysis needed further fractionation to reduce the polydispersity. This is done from solutions of the polymer in THF by careful addition of hexane and subsequent collection of the precipitate and repetition of the procedure on the residual solution. As a result, fractions of moderate polydispersity and degree of polymerization, DP, could be extracted (Fig. S4-S6).

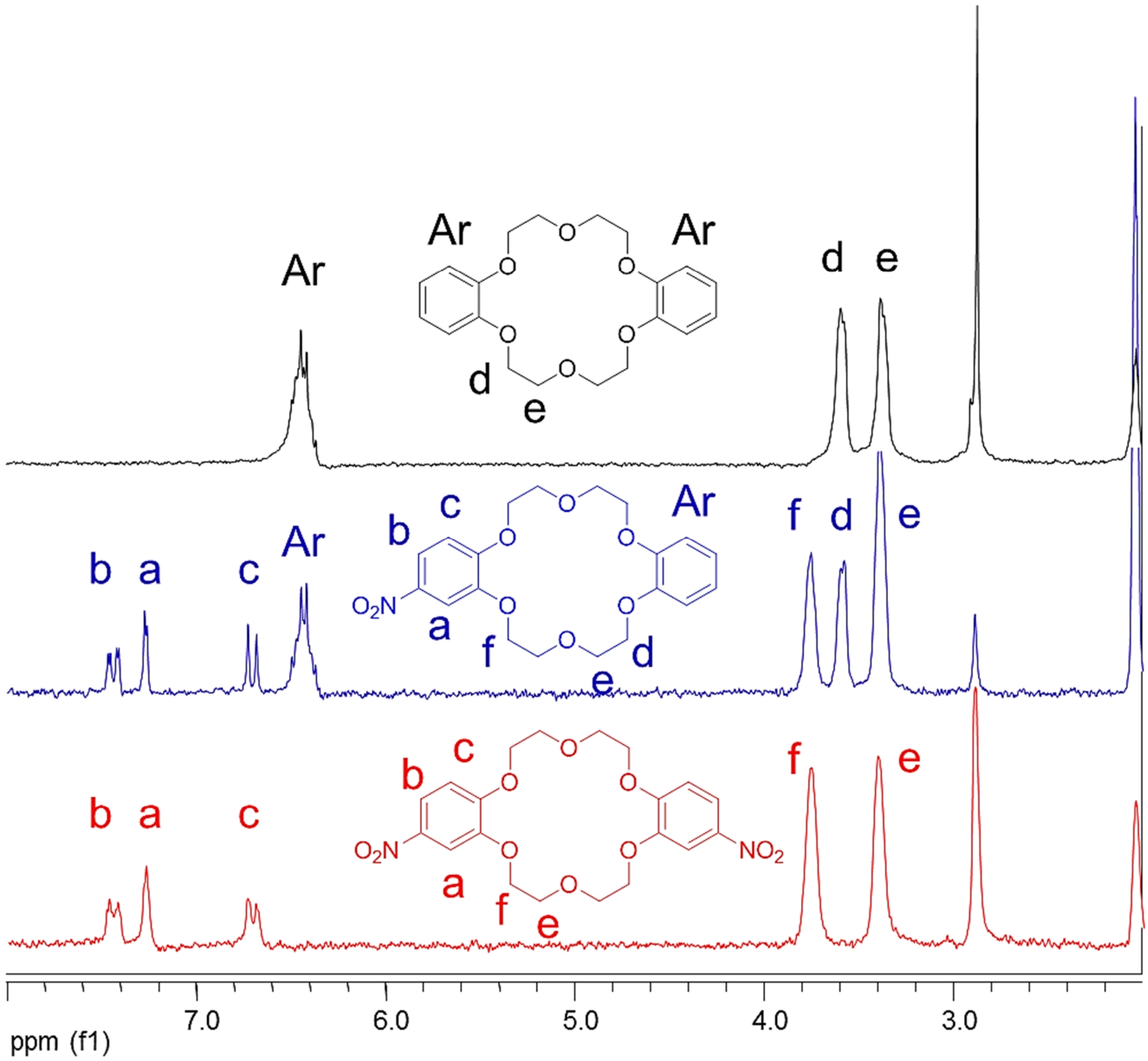

Fig. S2. Comparison of ^{1}H NMR spectra of nitro-derivatives and starting compound in DMSO-d_6.

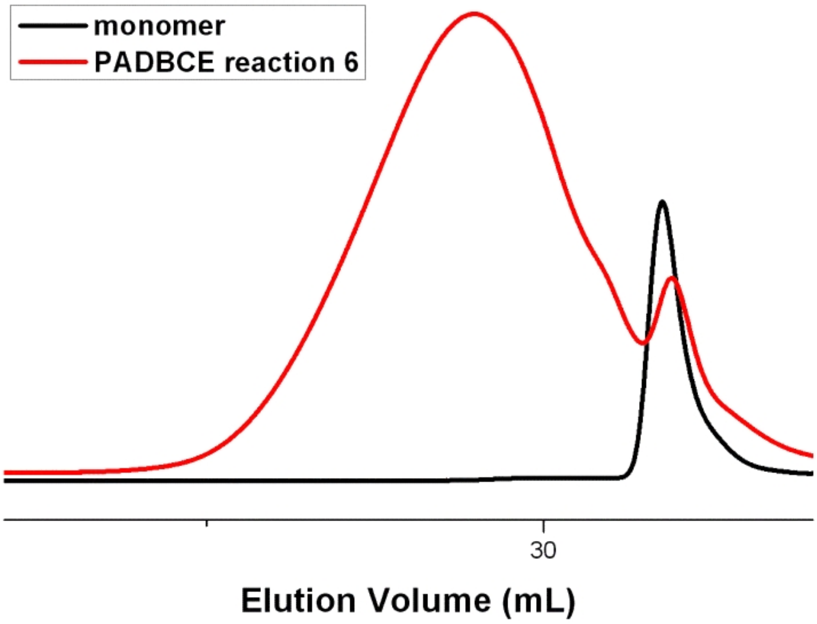

Fig. S3. SEC eluogram (DMF) of crude reaction mixture (red) and monomer (black) upon adjusting of coupling conditions.

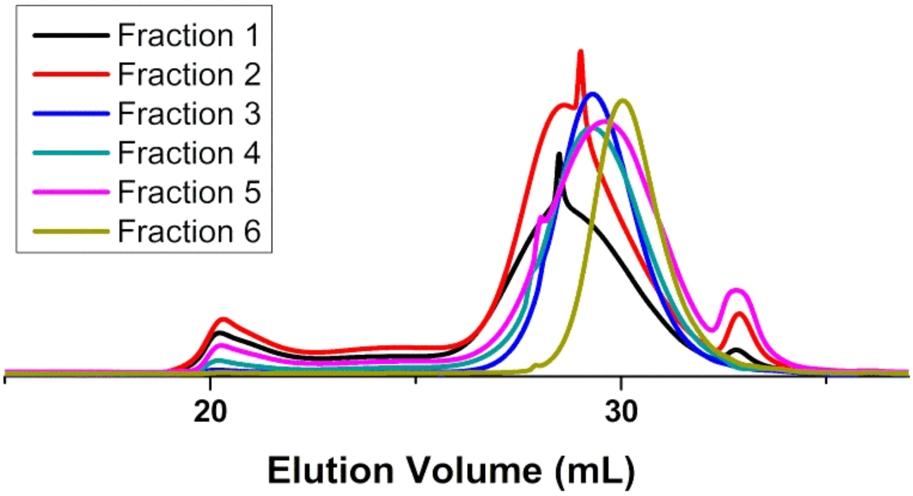

Fig. S4. SEC eluogram (DMF) of fractionation of the 4’,4’’-polymer.

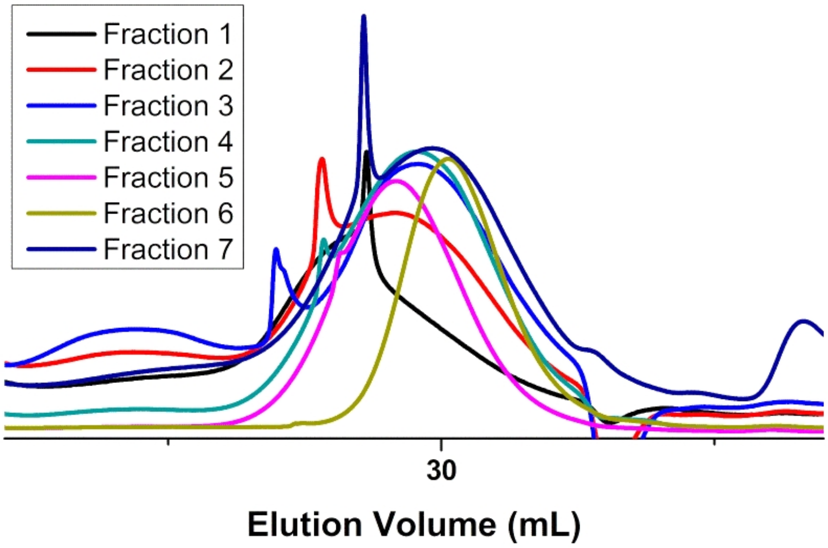

Fig. S5. SEC eluogram (DMF) of fractionation of the 4’,5’’-polymer.

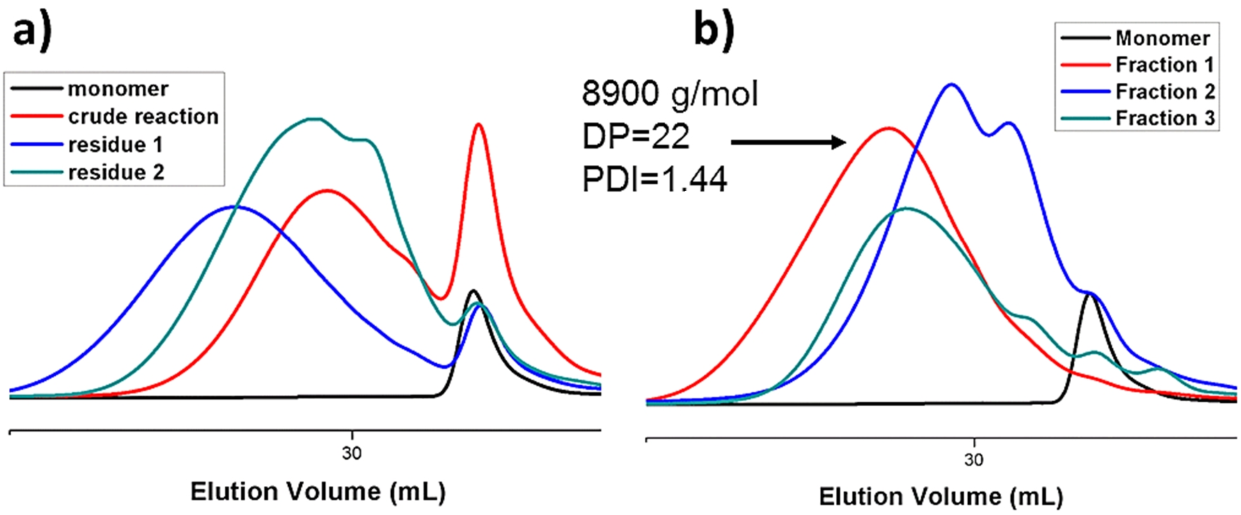

Fig. S6. Example of refractionation procedure. SEC eluograms (DMF) of the first fractionation (a) and the second one (b).

UV-Vis irradiation studies

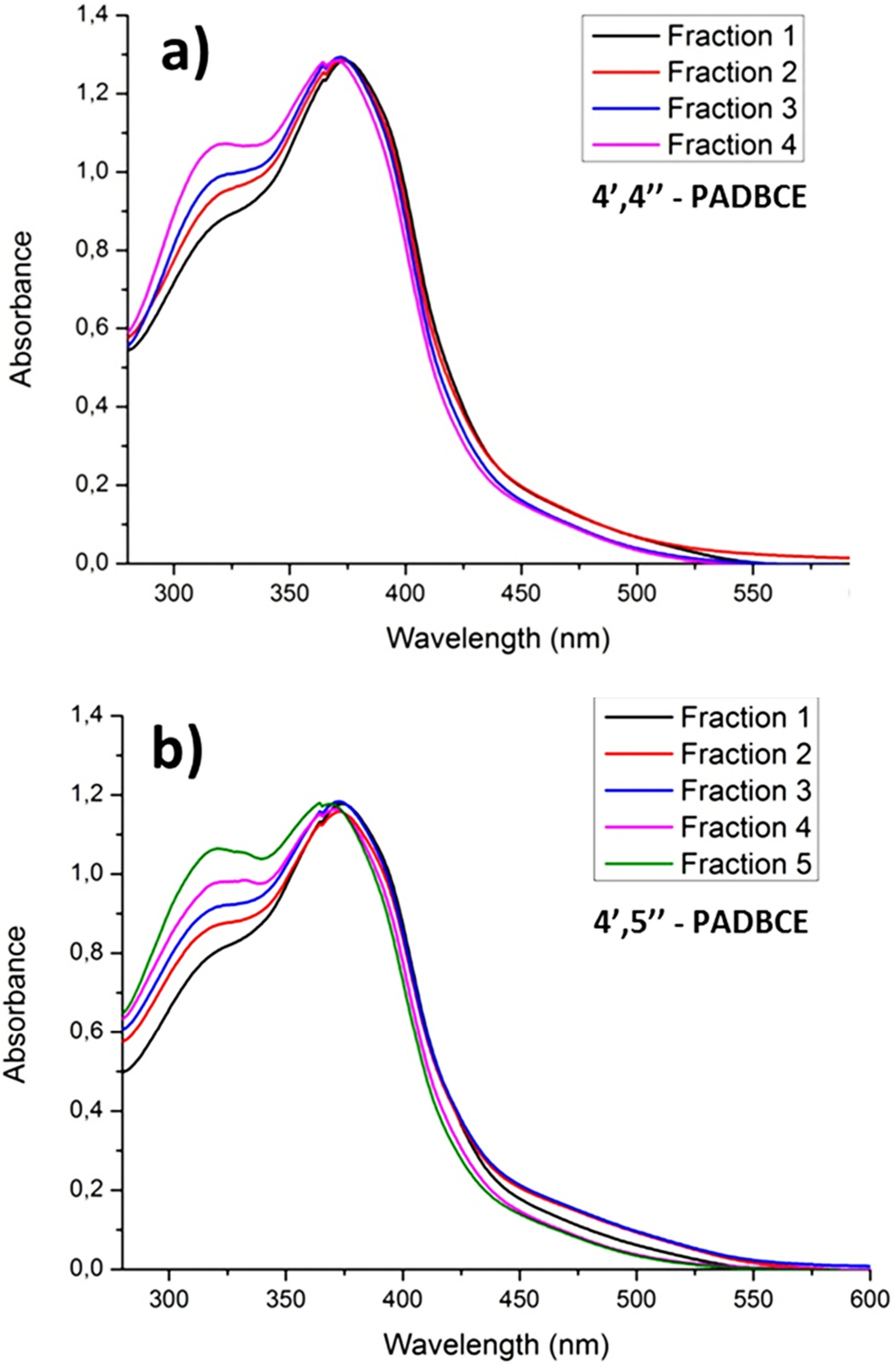

Fig. S7. UV-Vis spectra of different fractions of (a) 4',4''-poly(azodibenzo-18-crown-6-ether)s and (b) 4',5''-poly(azodibenzo-18-crown-6-ether)s (c=0.1 g/L in THF).

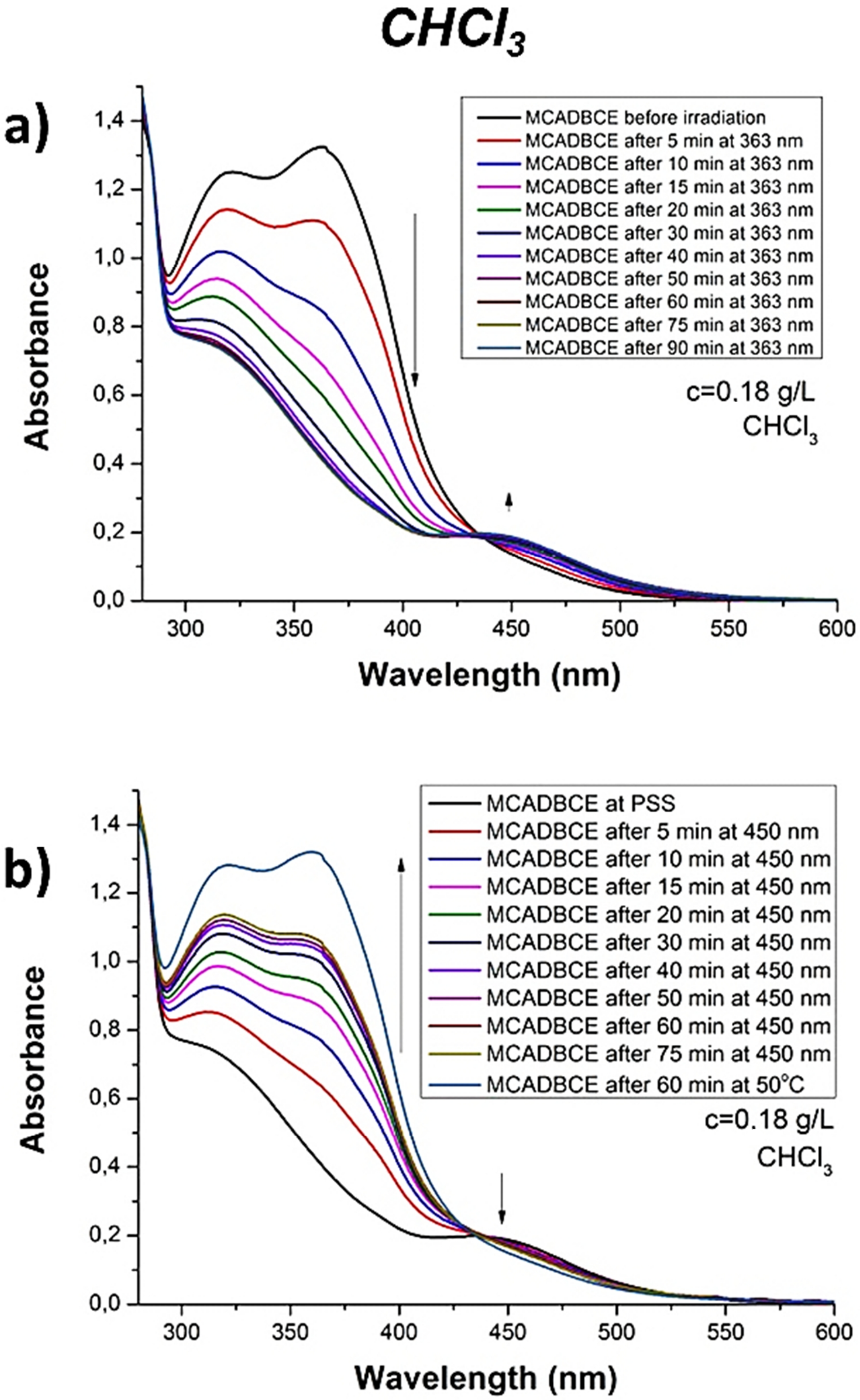

Fig. S8. UV-Vis absorbance spectra (280-600nm) of model compound, MC, (c=0.18 g/L) upon (a) *trans*-to-*cis* and (b) cis-to-trans photo-isomerisation in $CHCl_3$.

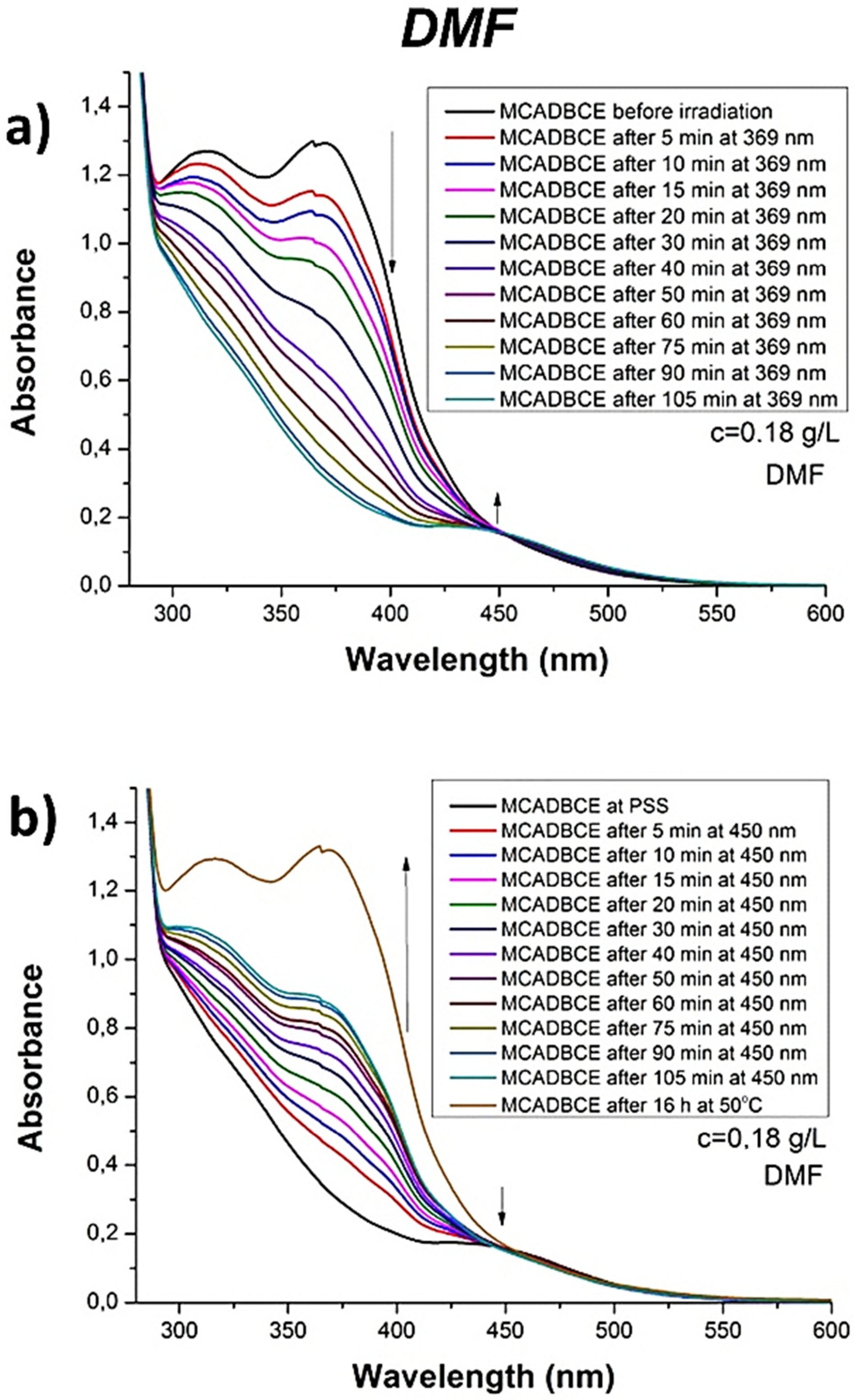

Fig. S9. UV-Vis absorbance spectra (280-600nm) of model compound, MC, (c=0.18 g/L) upon (a) *trans*-to-*cis* and (b) cis-to-trans photo-isomerisation in DMF.

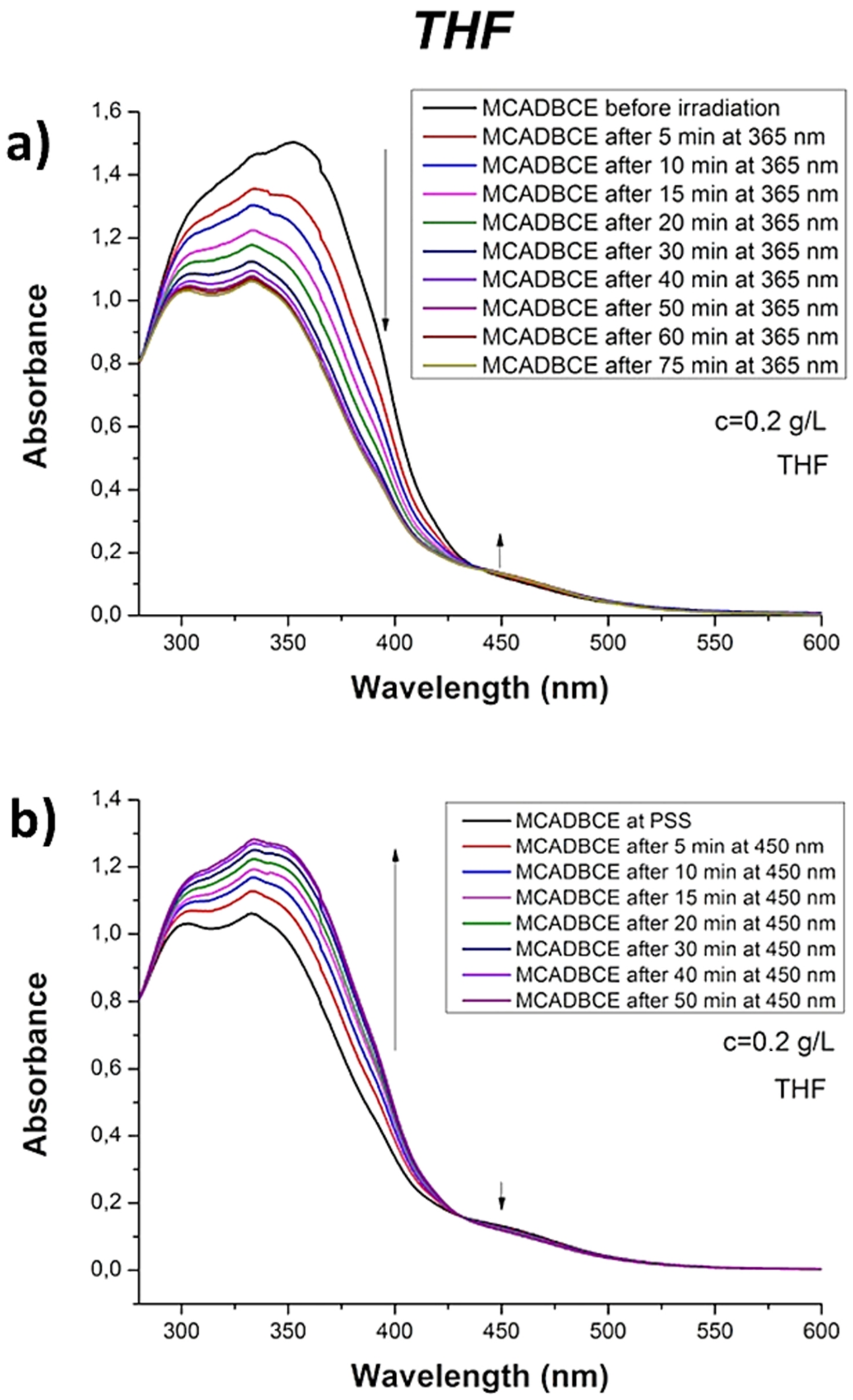

Fig. S10. UV-Vis absorbance spectra (280-600nm) of model compound, MC, (c=0.2 g/L) upon (a) *trans*-to-*cis* and (b) cis-to-trans photo-isomerisation in THF.

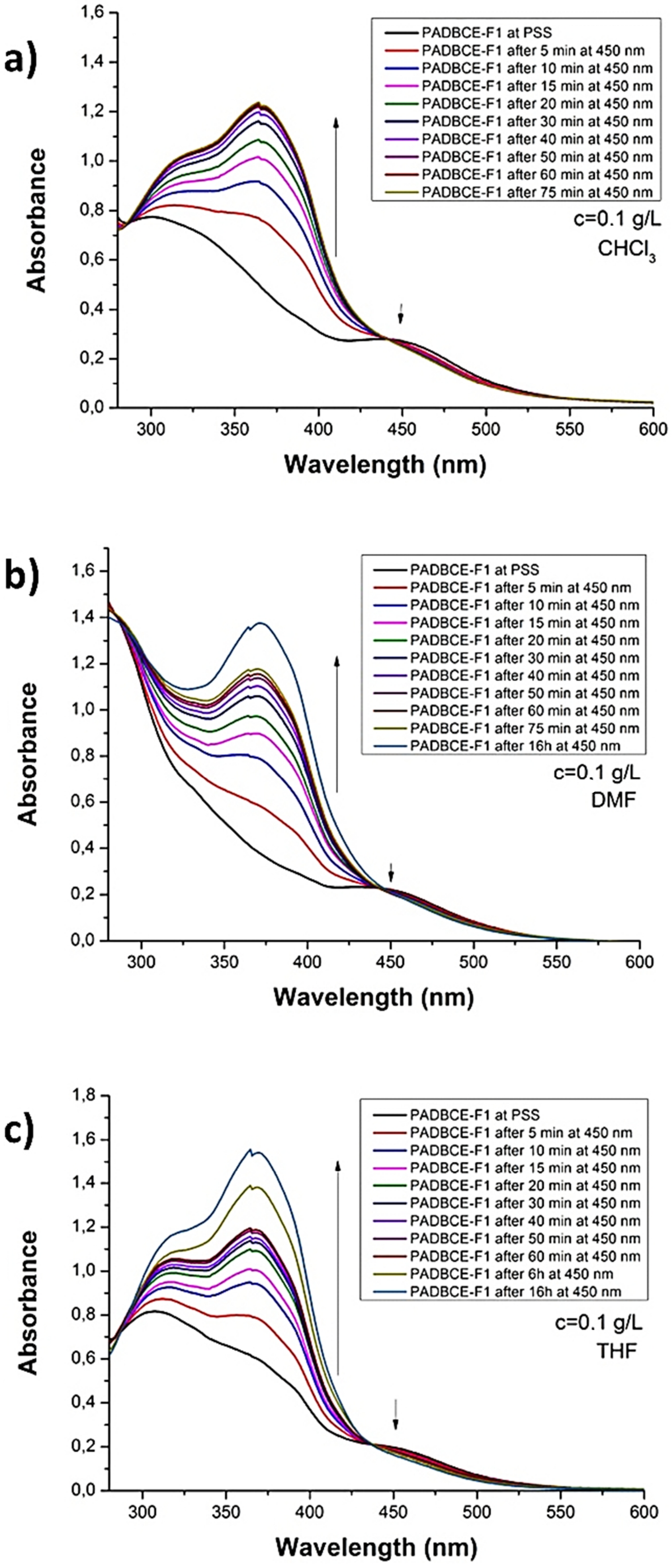

Fig. S11. UV-Vis absorbance spectra (280-600nm) of PADBCE-F1, (c=0.1 g/L) upon *cis*-to-*trans* photo-isomerisation in (a) $CHCl_3$; (b) DMF and (c) THF.

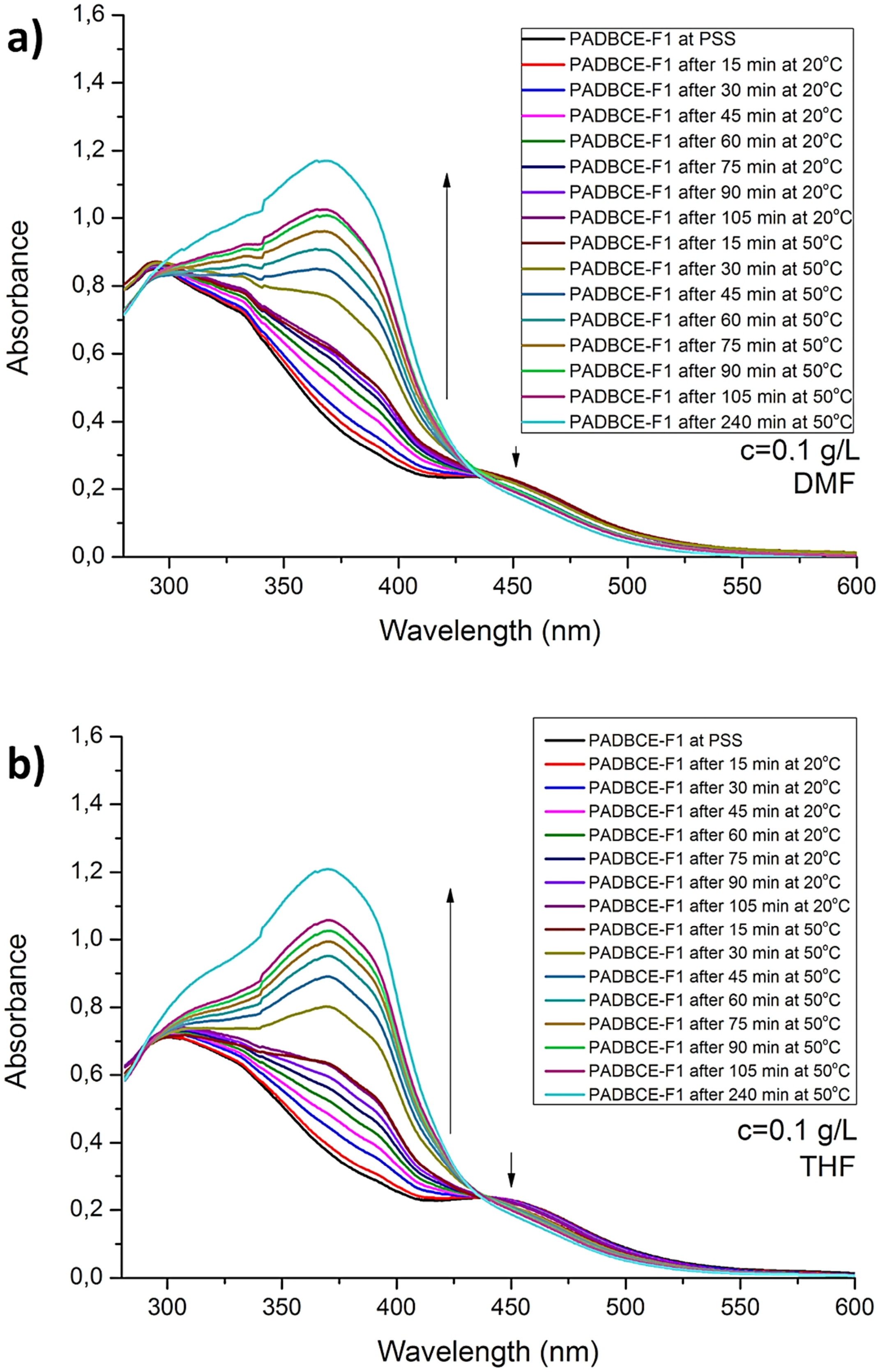

Fig. S12. Example of thermal relaxation of the polymers: UV-Vis spectra (280-600nm) of PADBCE-F1 (c=0.1 g/L) in (a) DMF and (b) THF at 20°C and 50°C.

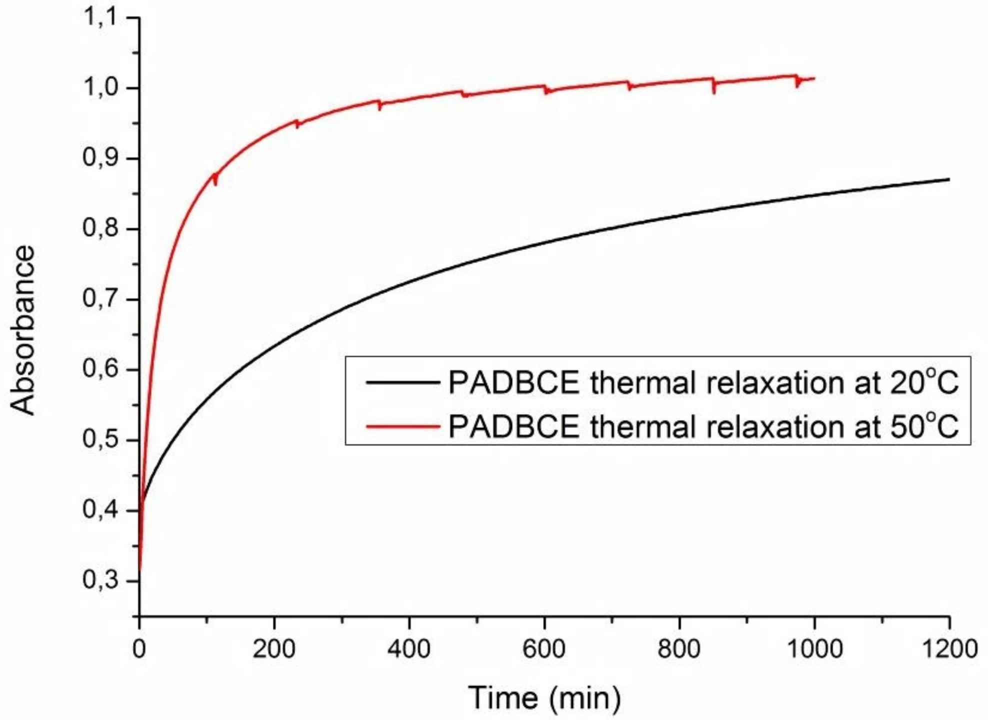

Fig. S13. Example of thermal relaxation of the polymers: Absorption at 363 nm as a function of time at 20°C (black) and 50°C (red) in chloroform for PADBCE-F1 (c=0.1 g/L).

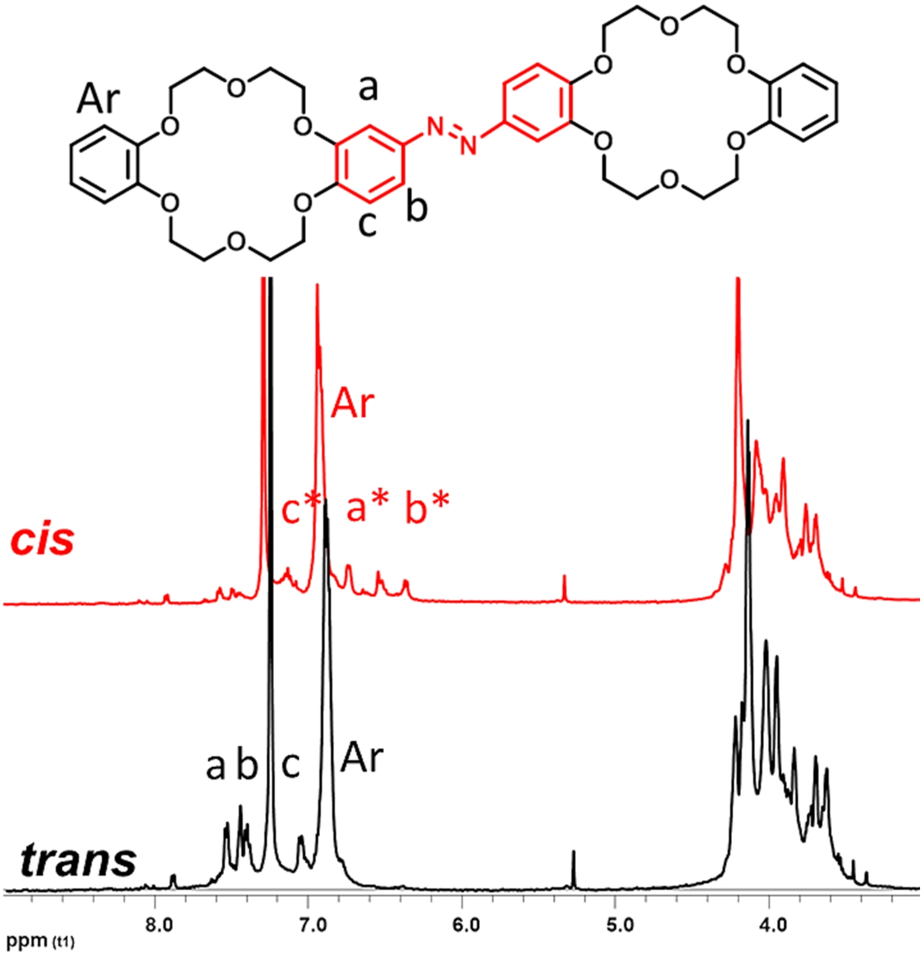

Fig. S14. ^{1}H NMR spectra of model compound, MC, in $CDCl_3$ in the *trans* and *cis* state. The structure of *trans*-azobis(dibenzo-18-crown-6-ether) is presented.

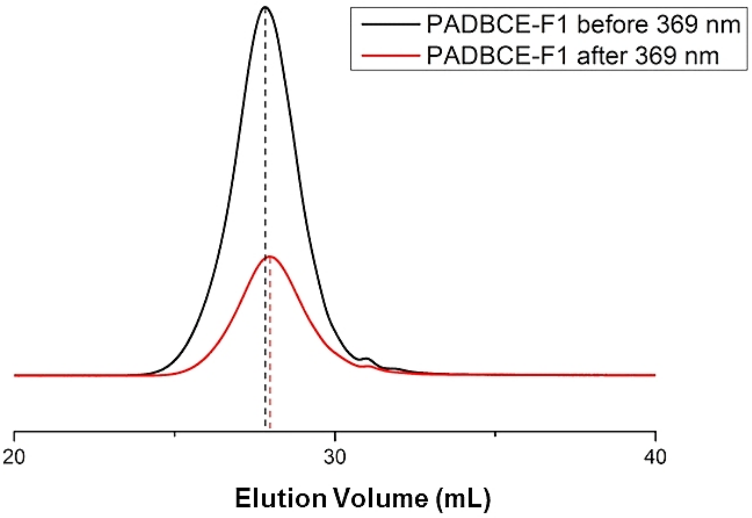

Fig. S15. Comparison of SEC eluograms (DMF) of PADBCE-F1 before (black) and after (red) irradiation.

Complex Formation Studies

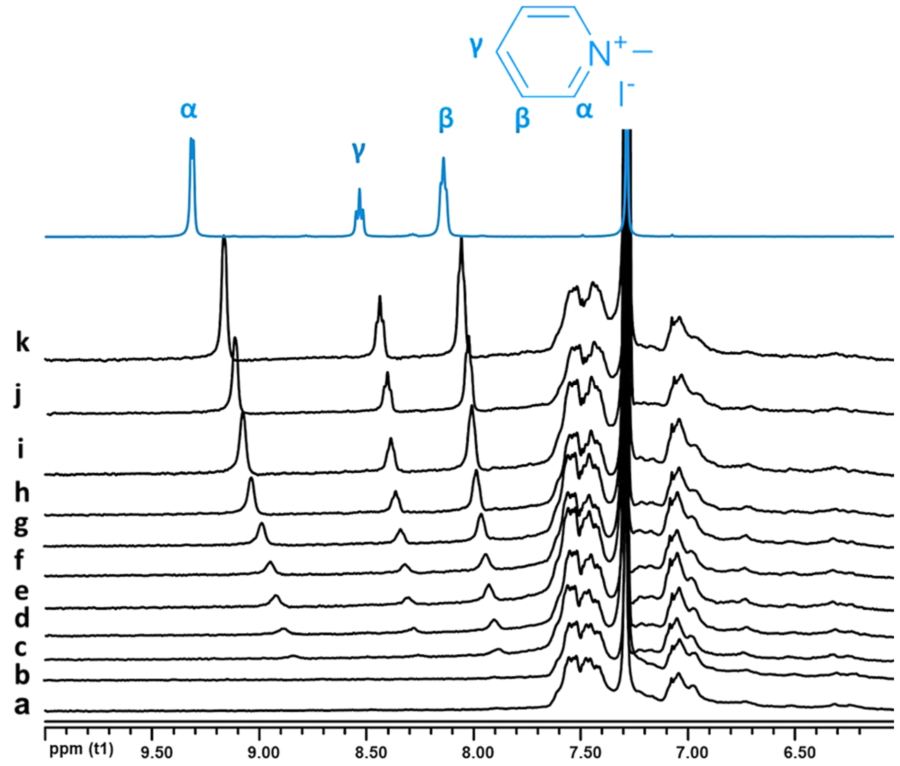

Fig. S16. Magnification (6-10 ppm) of ^{1}H NMR spectra of N-methyl pyridinium iodide, NMPI in $CDCl_3$ in the absence of host polymer (blue) and subsequent additions (a-k) to *trans* PADBCE-F2.

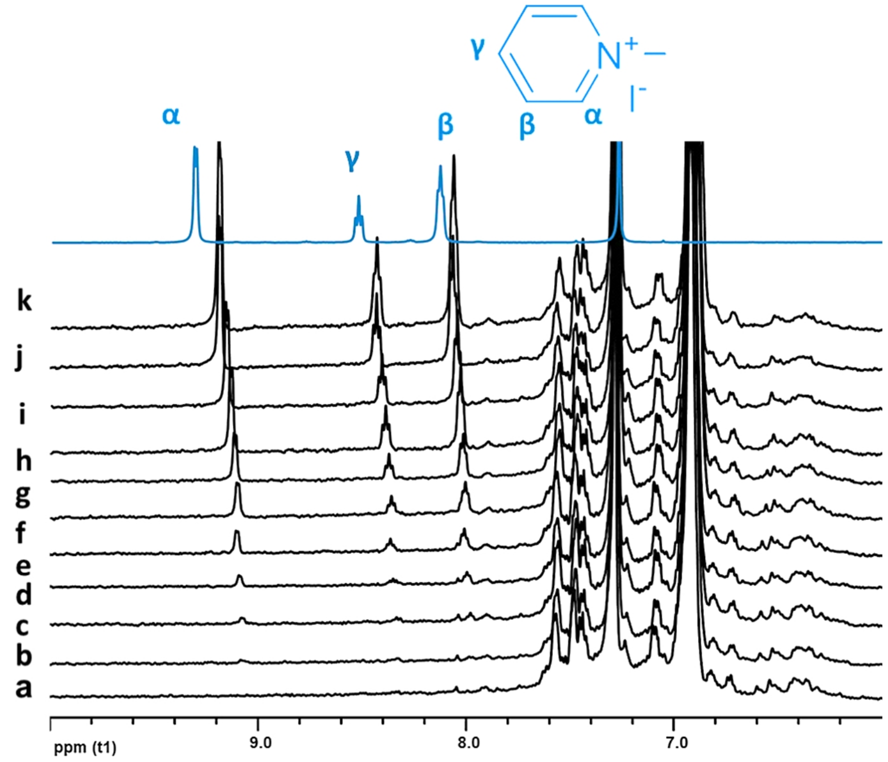

Fig. S17. Magnification (6-10 ppm) of ^{1}H NMR spectra of N-methyl pyridinium iodide, NMPI in $CDCl_3$ in the absence of model compound, MC (blue) and subsequent additions (a-k) to *trans* MC.

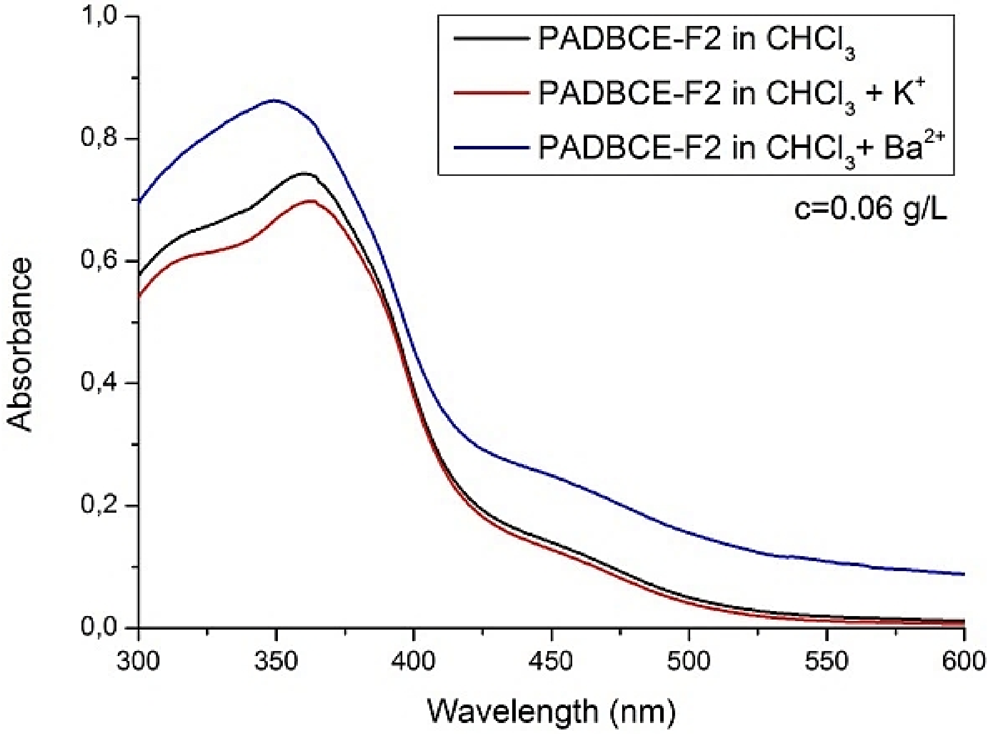

Fig. S18. UV-Vis spectra (280-600nm) of PADBCE-F2 in chloroform upon addition of K^+ and Ba^{2+} ions (c=0.02 g/L). Note: Precipitation of the Ba^{2+} sample occurs, which is evidenced by anomaly in baseline.

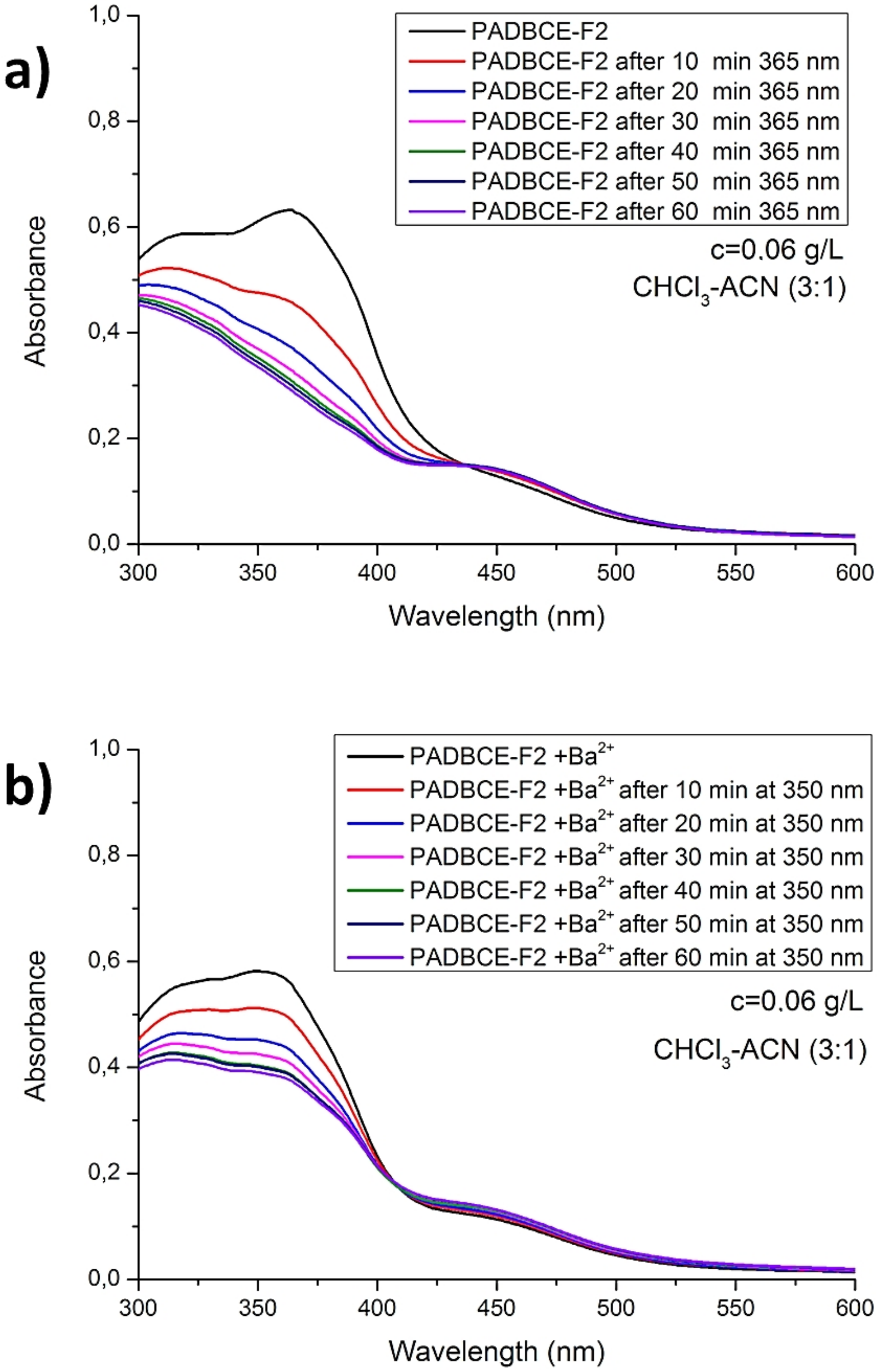

Fig. S19. UV-Vis spectra (280-600nm) of *trans*-to-*cis* photoisomerization of PADBCE-F2 in 25% ACN-$CHCl_3$ without (a) and upon addition of Ba^{2+} ions (b).

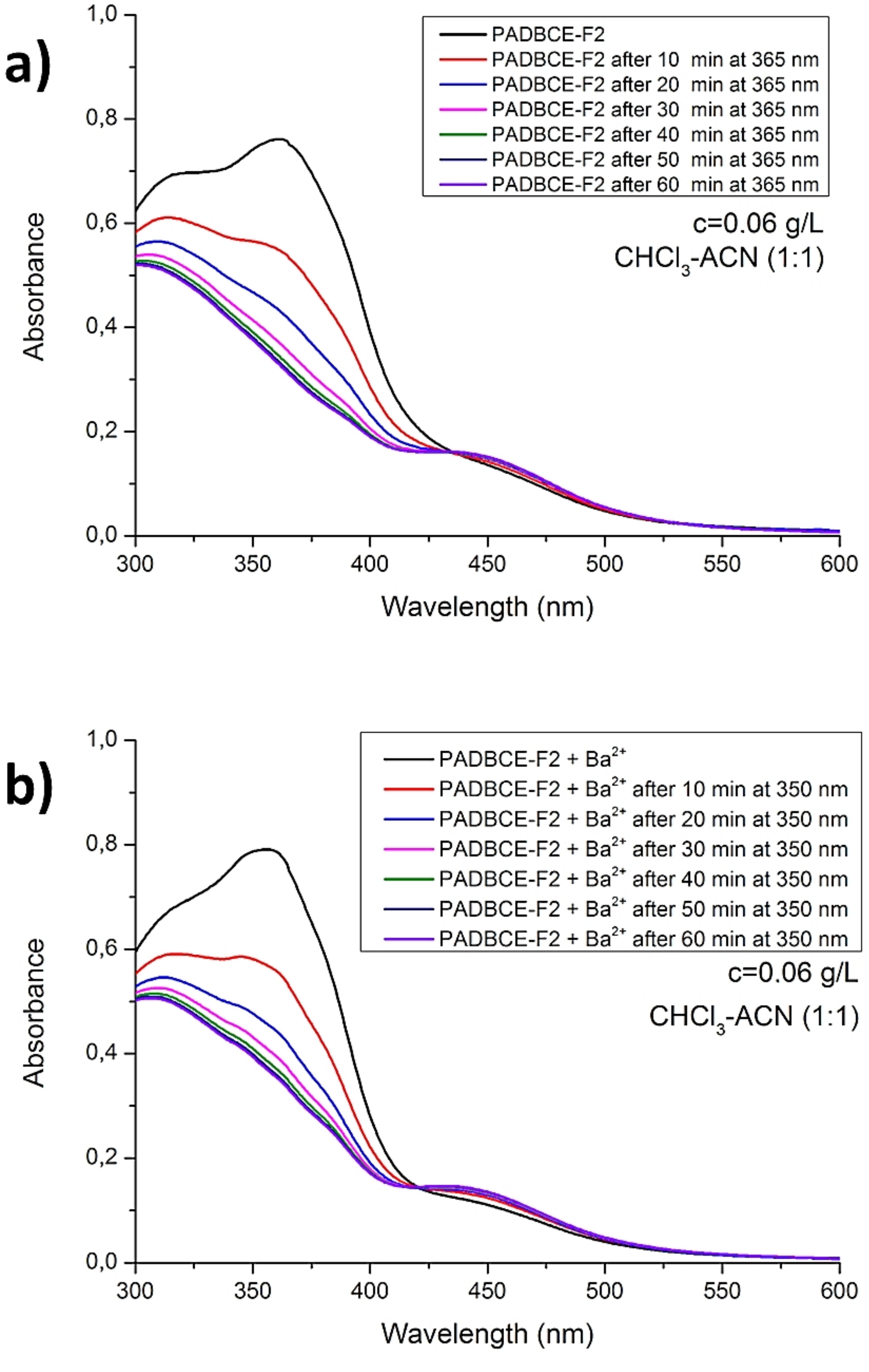

Fig. S20. UV-Vis spectra (280-600nm) of *trans*-to-*cis* photoisomerization of PADBCE-F2 in 50% ACN-$CHCl_3$ without (a) and upon addition of Ba^{2+} ions (b).

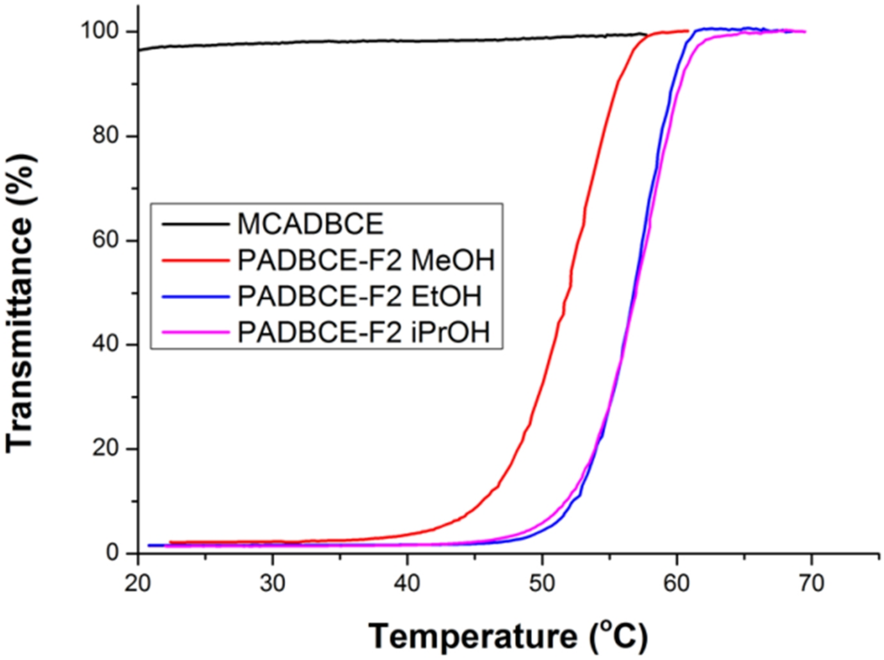

Fig. S21. Transmittance *vs.* Temperature plots for PADBCE-F2 and model compound in different alcohols at 2 g/L (cooling rate 1 °C/min).

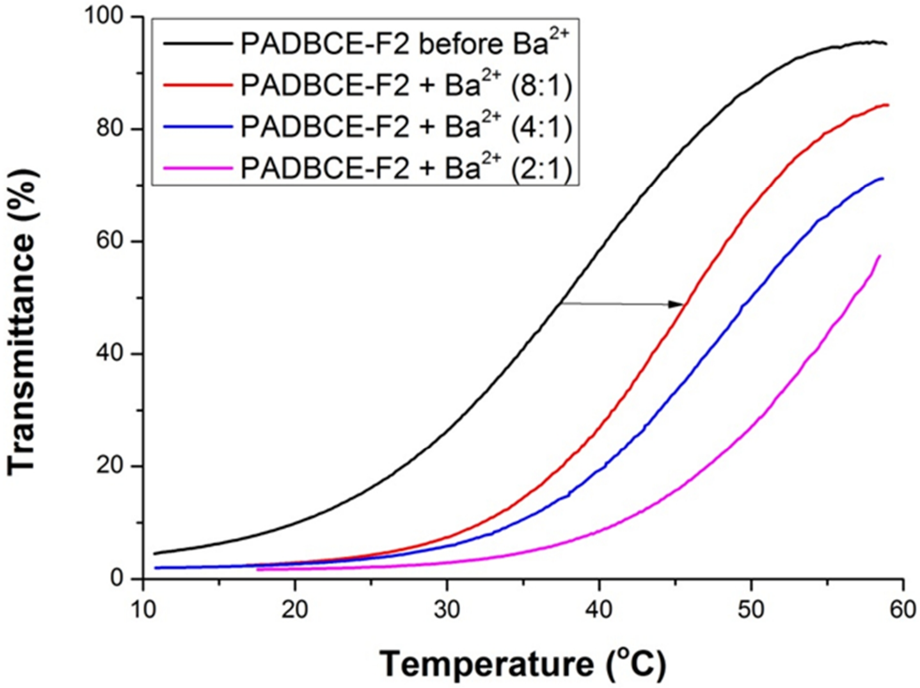

Fig. S22. Transmittance *vs.* Temperature plots for PADBCE-F2 in methanol (1 g/L) (cooling rate 2 °C/min).

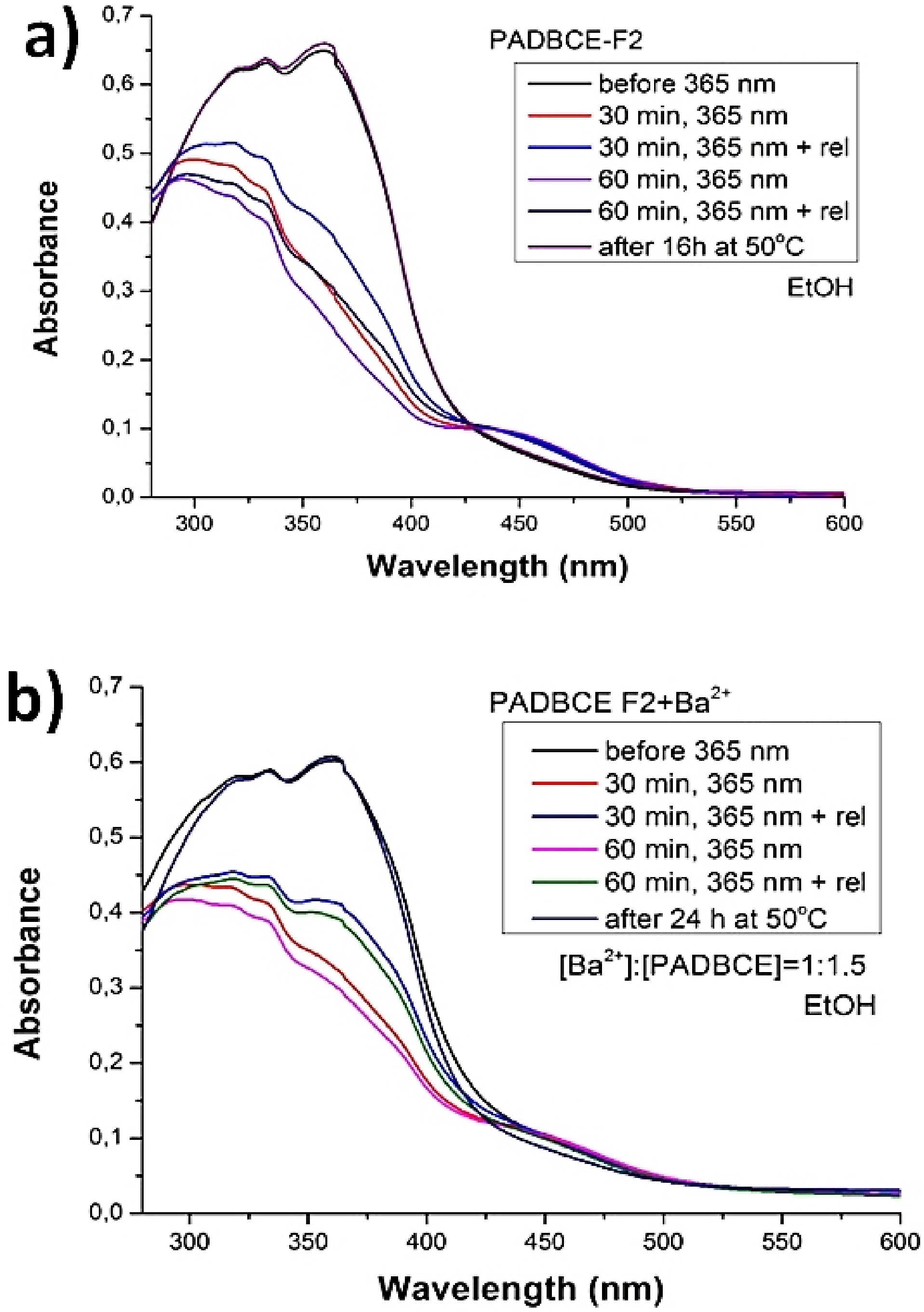

Fig. S23. UV-Vis spectra upon trans-to-cis photoisomerisation of PADBCE-F2 in ethanol (0.5 g/L) in the absence (a) and presence (b) of barium ions.