Supporting Information

On the Relation of Energy and Electron Transfer in Multidimensional Chromophores Based on Polychlorinated Triphenylmethyl Radicals and Triarylamines

Markus Steeger,^a Stefanie Griesbeck,^a Alexander Schmiedel,^a Marco Holzapfel,^a Ivo Krummenacher,^b Holger Braunschweig^b and Christoph Lambert^{*a}

^a Institut für Organische Chemie, Universität Würzburg, and Center for Nanosystems Chemistry, Am Hubland,
 97074 Würzburg, Germany. Fax: (+49) 931/31-87218; E-mail: <u>christoph.lambert@uni-wuerzburg.de</u>
 ^b Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

Synthesis

The compounds **HAB-S** and **HAB-A** were synthesised by dicobaltoctacarbonyl catalysed cyclotrimerisation of the tolan derivative **6** (Fig. S1).



Fig. S1 Synthesis of HAB-S, HAB-A and HAB-Model.

The cyclotrimerisation reaction is sensible to the steric demands of the arene substituents in *ortho*-position to the acetylene group. Therefore we chose the polychlorinated triarylmethane radical **A** as electron poor redox centre.¹ Cyclotrimerisation attempts of structurally similar molecules with the fully perchlorinated acceptor centre \mathbf{B}^2 with $Co_2(CO)_8$ and $CpCo(CO)_2$ were not successful.



The cyclotrimerisation of tolan 6 yielded a symmetric (HAB-S) and an asymmetric isomer (HAB-A) in a ratio of 1:5.3. The isomer ratio obtained differs considerably from the expected statistical value of 1:3.¹ This can be explained by a distinct difference in the sterical demand of the two acetylene substituents in tolan 6 which favours an asymmetrical oxidative coupling within the catalytic cycle.¹ The tolan derivative $\mathbf{6}$ was obtained by Sonogashira coupling of tris(2,4,6-trichlorophenyl)methane N,N-di(4-methoxyphenyl)-N(4the known and (ethynyl)phenyl)amine. Although several very reactive catalysts for coupling of chlorinated arenes are described in literature the difficulty of the present synthesis was the required selectivity. It turned out that the catalytic systems either were not reactive enough (e.g. Pd(PPh₃)₂Cl₂, CuI)³ or too reactive (e.g. Pd(PPh₃)₄, P(t-Bu)₃, CsCO₃, DBU⁴ or Pd(MeCN)₂Cl₂, x-Phos, CuI⁵) as multiple reactions and side reactions presumably at the chloro substituents in ortho-position to the methane centre could be observed. The latter by-products could only be separated by size exclusion gel permeation chromatography as solubility and polarity of the isomers are very similar. For the synthesis of 6 the optimised reaction conditions proved to be stirring N_{N} -di(4-methoxyphenyl)-N(4-(ethynyl)phenyl)amine (2 equiv.), tris(2,4,6-trichlorophenyl)methane (1 equiv.), Cs₂CO₃, DBU, Pd(PPh₃)₂Cl₂, and P(t-Bu)₃ in DMF at 150 °C (800 W) in a microwave oven for 8 min according to the procedure by Huang et al. which gave 6 in 30% yield.⁴

The model compound **9** was synthesised by a Diels-Alder reaction of the tolan derivative **6** with tetraphenylcyclopentadienone. All α -H compounds of this series (**7**, **8** and **9**) showed complex NMR spectra. Although the overall peak integrals were matching to the different type of atoms the assignment of the signals was impossible due to an excessive number of signals and complex splitting patterns. We assume that the steric demand induced by the HAB framework to the pyramidal polychlorinated triarylmethane centres generates stereoisomers that cannot interconvert rapidly on the NMR time scale at rt. In order to provoke rapid equilibration of all these isomers and, thus, to simplify the NMR spectra, temperature dependent NMR measurements were performed in dimethylsulfoxide[d₆], 1,1,2,2-tetrachloroethane[d₂], 1,2-dichlorobenzene[d₄] and acetone[d₆] from rt up to 353 K. With increasing temperature some signals coalesced but the coalescence point could not be exceeded in the used solvents (see Fig S3-15 for the temperature dependent spectra in acetone[d₆]). Although we could not obtain simplified NMR spectra, the observed coalescence indicates that the origin of the complex NMR spectra are most likely stereoisomers.

The last step in the synthetic approach to **HAB-S**, **HAB-A** and **HAB-Model** is the radicalisation of the α -H compounds **7**, **8** and **9**. In this process, the α -H compounds were first deprotonated by tetrabutylammonium hydroxide (TBAOH) and then oxidised by *p*-chloranil. In each case a reaction time of 2 days was crucial to ensure maximum conversion. NMR analysis of **HAB-S**, **HAB-A** and **HAB-Model** was prevented by the paramagnetic character of the PCTM centres, resulting in line-broadening. The presence of stereoisomers could therefore not be clarified in case of the radicals. However, as the geometry of the polychlorinated triarylmethane centres changed from pyramidal to trigonal planar upon radicalisation, the sterical demand of neighbouring centres should thereby be decreased disfavouring the formation of stereoisomers. The degree of radicalisation was determined to be ≥ 95 % by comparison of the oxidation and reduction peaks in the square-wave voltammograms.

The star-like oligomer **10** was synthesised by *Sonogashira* coupling of tris(2,4,6-trichlorophenyl)methane and *N*,*N*-di(4-methoxyphenyl)-*N*(4-(ethynyl)phenyl)amine similar to the synthesis of the tolan derivative **6** (Fig. S2).



Fig. S2 Synthesis of Star-Model and Star.

Thereby, the addition of *N*,*N*-di(4-methoxyphenyl)-*N*(4-(ethynyl)phenyl)amine was carried out in three consecutive steps each with at most four equivalents. The best reaction conditions gave yields of 34 % and consist of $Pd(MeCN)_2Cl_2$, x-Phos and CuI as described by Langer et al.⁵ Radicalisation of **10** was performed in the same manner as described above. The degree of radicalisation in case of **Star** was determined to be 90 %. However, the remaining starting material in the sample should not affect the spectroscopic evaluation of the charge transfer properties. The latter exhibits no absorption in the range of the IV-CT transition of **Star** (see absorption section) and thus can be neglected in the following investigations. **Star-Model** was synthesised by deprotonating **6** with TBAOH and oxidation with AgNO₃ to achieve a 97 % degree of radicalisation.

Synthetic protocols

All reagents were purchased from commercial suppliers in standard quality and used as received. Reactions under a nitrogen-atmosphere were carried out in flame-dried Schlenk vessels and the solvents were dried according to common literature procedures.³³ Silica gel (32-63 μ m) was obtained from Merck. *N,N*-Di(4-methoxyphenyl)-*N*(4-(ethinyl)phenyl)amine was synthesised according to a literature procedure.⁸ Melting points were measured with a Tottoli melting point apparatus (Büchi) and are uncorrected. Gel permeation chromatography (GPC) was conducted at rt on a Shimadzu instrument (Model SPD-M20A diode array detector, CBM-20A system controller, LC-20AD solvent delivery unit, DGU 20A9 online degasser) in recycling mode with two SDV columns (PSS SDV preparative 50 Å and 500 Å, dimension 20 x 600 mm, particle size 10 μ m). The NMR data were recorded on a Bruker 600 DMX FT spectrometer. For compounds containing many chlorine atoms the mass signals were distributed over a broad m/z region so that the signal to noise ratio of the monoisotopic signal was too low for an accurate mass measurement. In these cases the most intensive signals (X + n) of the isotropic distribution were checked against values calculated with the software module "Bruker Daltonics IsotopePattern" of the software Compass 1.1 (Bruker Daltonik GmbH, Bremen, Germany).

General Procedure (GP): Radicalisation of polychlorotriphenylmethanes: Under a nitrogen atmosphere the polychlorotriphenylmethane was dissolved in absolute THF (10 ml) and degassed. TBAOH (1 M solution in water, 2.33 equiv per reaction centre) was added and the dark blue mixture stirred at rt under exclusion of light for 3 d. Thereafter *p*-chloranil (5.50 equiv per reaction centre) was added and the now brown solution was stirred under exclusion of light at rt for further 3 d. The reaction mixture was poured in 2 N HCl (50 ml) and extracted with CHCl₃ (30 ml). The organic phase was dried over MgSO₄ and the solvent removed in vacuo. The crude product was purified by gel permeation chromatography (Chloroform).

HAB-S (1)

Radical **1** was synthesised according to GP from **7** (45 mg, 18 μ mol). **1** (18 mg, 7.2 μ mol, 40 %) was obtained as a brown solid. SWV measurements proved a degree of radicalisation of 95 %. HRMS (ESI): [M⁺+10] calc.: 2537.78172 m/z, found: 2537.78130 *m*/*z*, Δ =0.17 ppm.

HAB-A (2)

Radical **2** was synthesised according to GP from **8** (40 mg, 16 μ mol). **2** (31 mg, 13 μ mol, 78 %) was obtained as a brown solid. SWV measurements proved a degree of radicalisation of 95 %. HRMS (ESI): [M⁺+10] calc.: 2537.78172 m/z, found: 2537.77993 *m*/*z*, Δ =0.71 ppm.

HAB-Model (3)

Radical **3** was synthesised according to GP from **9** (60 mg, 50 μ mol). **2** (33 mg, 28 μ mol, 55 %) was obtained as a brown solid. SWV measurements proved a degree of radicalisation of 99 %. HRMS (ESI): [M⁺] calc.: 1198.08748 m/z, found: 1198.08850 *m*/*z*, Δ =0.85 ppm.

Star (4)

Radical **4** was synthesised according to GP from **10** (36 mg, 25 μ mol). **2** (16 mg, 11 μ mol, 44 %) was obtained as a brown solid. SWV measurements proved a degree of radicalisation of 90 %. HRMS (ESI): [M⁺] calc.: 1428.26078 m/z, found: 1428.26170 m/z, Δ =0.64 ppm.

Star-Model (5)

Under a nitrogen atmosphere **6** (68 mg, 80 μ mol) was dissolved in absolute THF (30 ml), TBAOH (1.5 M, 1.00 ml, 1.50 mmol) was added and the reaction mixture was stirred at rt under light exclusion over night. Afterwards the violet solution was poured in a hexane (30 ml), water (30 ml) mixture. The organic phase was separated and the solvent removed in vacuo. Under a nitrogen atmosphere the residue was dissolved in absolute DCM (10 ml). AgNO₃ (15 mg, 88 μ mol) was added and the reaction mixture was stirred at rt under light exclusion for 5 h. The brown solution was directly filtrated through silica gel (DCM) to obtain **5** (30 mg, 35 μ mol, 44 %) as a brown solid. SWV measurements proved a degree of radicalisation of 97 %. HRMS (ESI): [M⁺] calc.: 841.93098 *m/z*, found: 841.93138 *m/z*, Δ =0.48 ppm.

4-((4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)ethynyl)-N,N-bis(4-methoxyphenyl)aniline (6) Under a nitrogen atmosphere N,N-Di(4-methoxyphenyl)-N(4-(ethinyl)phenyl)amine (119 mg, 361 µmol), tris(2,4,6-trichlorophenyl)methane (100 mg, 180 µmol), Cs₂CO₃ (129 mg, 397 µmol) and DBU (27.0 µl, 180 µmol) were dissolved in a quartz pressure vessel in absolute DMF (5 ml) and degassed. After addition of $Pd(PPh_3)_2Cl_2$ (4 mg, 5 µmol) and P(t-Bu)₃ (1 M in toluene, 11 µl, 11 µmol) the reaction mixture was stirred at 150 °C in a microwave oven for 8 min. After cooling, EA was added to reaction mixture and then washed with saturated NaCl solution (3 x 30 ml). The combined aqueous phases were extracted with EA (3 x 30 ml) and the combined organic phases dried over MgSO₄. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel with (DCM/petrol ether 1:3). The crude product was purified further by gel permeation chromatography (Chloroform) to get pure 4 (46 mg, 54 µmol, 30 %) as a yellow solid. M.p. 258 °C; ¹H NMR (600 MHz, acetone[d₆], 298 K): δ [ppm]=7.63 (d, ⁴J_{HH} = 2.3 Hz, 2 H), 7.59 (d, ⁴J_{HH} = 1.7 Hz, 1 H), 7.46 (d, ${}^{4}J_{HH} = 1.4 \text{ Hz}, 2 \text{ H}), 7.43 \text{ (d, }{}^{4}J_{HH} = 1.7 \text{ Hz}, 1 \text{ H}), 7.35 \text{ (AA', 2 H)}, 7.13 \text{ (AA', 4 H)}, 6.96 \text{ (BB', 4 H)}, 6.79 \text{ (s, 1 H)}, 6.79 \text{ (s, 1$ 6.77 (BB', 2 H), 3.81 (s, 6 H); ¹³C NMR (150.9 MHz, acetone[d₆], 298 K): δ [ppm]=158.0, 150.8, 140.4, 138.8, 138.7, 138.00, 137.98, 137.92, 137.3, 135.3, 135.1, 134.71, 134.69, 133.6, 133.2, 131.5, 130.90, 130.87, 129.37, 129.35, 128.6, 126.4, 118.6, 115.9, 112.6, 94.6, 85.6, 55.8, 51.1, no carbons at the chlorinated benzene rings are chemical equivalent with the exception of one pair; HRMS (ESI): $[M^+]$ calc.: 842.93880 m/z, found: 842.93884 m/z, Δ =0.05 ppm.

1,3,5-Tris{4-[*N*,*N*-di(4-methoxyphenyl)amino]phenyl}-2,4,6-tris[4-(bis(2,4,6-trichlorophenyl)methyl)-3,5dichlorophenyl]benzol (7) and 1,2,4-Tris{4-[*N*,*N*-di(4-methoxyphenyl)amino]phenyl}-3,5,6-tris[4-(bis(2,4,6-trichlorophenyl)amino]phenyl]-3,5,6-tris[4-(bis(2,4,6-trichlorophenyl)amino]phenyl]-3,5,6-tris[4-(bis(2,4,6-trichlorophenyl)amino]phenyl]-3,5,6-tris[4-(bis

trichlorophenyl)methyl)-3,5-dichlorophenyl]benzol (8)

To a degassed solution of **6** (155 mg, 0.182 mmol) in 1,4-dioxane (5 ml) dicobaltoctacarbonyl (6.0 mg, 0.02 mmol) was added and the reaction mixture stirred at 100 °C for 4 d. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel DCM/petrol ether $(1:2\rightarrow1:1\rightarrow2:1)$ and by gel permeation chromatography (THF). The pure HAB **7** (12 mg, 4.9 µmol, 8 %) was obtained as a yellow solid. ¹H NMR

(600 MHz, acetone[d₆], 323K): δ [ppm]=7.56 (3H), 7.46-7.43 (3H), 7.41 (3H), 7.28-7.26 (3H), 7.05-6.60 (45 H),3.78-3.77 (18H); ¹³C NMR (150.9 MHz, acetone[d₆], 323K): δ [ppm]=156.6-156.5, 148.0, 143.0-142.9, 142.1-142.0, 141.9-141.7, 139.1-139.0, 138.7-138.5, 138.0-137.9, 137.8-137.7, 136.3-136.2, 135.8, 135.4, 135.3-135.2, 134.5-134.0, 132.4-133.2, 131.1-130.9, 130.7, 129.6-129.4, 129.2, 126.5-126.1, 123.4-122.9, 115.6-115.4, 55.7-55.6, 51.0, the existence of an unknown number of conformers causes the observation of signals of higher order; HRMS (ESI): [M⁺+12] calc.: 2540.80520 *m*/*z*, found: 2540.80117 *m*/*z*, Δ =1.59 ppm. The pure HAB **8** (64 mg, 25 µmol, 42 %) was obtained as a yellow solid. ¹H NMR (600 MHz, acetone[d₆], 313K): δ [ppm]=7.58-7.53 (3H), 7.48-7.17 (8H), 7.12-6.57 (46 H), 3.78-3.76 (18H); ¹³C NMR (150.9 MHz, acetone[d₆], 313K): δ [ppm]=156.9-156.7, 148.1-147.9, 143.4-141.7, 140.0-137.5, 137.1-135.0, 134.7-134.2, 133.6-132.5, 131.1-130.6, 129.7-129.0, 126.9-126.4, 123.3-123.0, 122.1-121.8, 115.7-115.5, 55.8, 51.2-51.1, the existence of an unknown number of conformers causes the observation of an unknown number of conformers causes the observation of an unknown number of conformers causes Δ (ESI): Δ =1.64 ppm.

1-{4-[*N*,*N*-di(4-methoxyphenyl)amino]phenyl}-2-[4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl]-3,4,5,6-tetraphenylbenzol (9)

Under a nitrogen atmosphere **6** (150 mg, 180 μ mol) and tetraphenylcyclopentadienone (68.0 mg, 180 μ mol) were dissolved in diphenyl ether (15 ml) and stirred at reflux for 3 d. After cooling, the residue was purified by flash chromatography on silica gel DCM/petrol ether (1:2). The pure compound **9** (65 mg, 56 μ mol, 31 %) was obtained as a yellow solid. ¹H NMR (600 MHz, acetone[d₆], 323K): δ [ppm]=7.52 (1.4 H), 7.38-7.35 (2H), 7.20-7.19 (0.5 H), 6.97-6.73 (31.6 H), 6.67-6.66 (0.7 H), 6.59-6.49 (3 H), 3.77-3.75 (6 H), due to the existence of at least two conformers, fractional integrals are observed; ¹³C NMR (150.9 MHz, acetone[d₆], 313K): δ [ppm]=156.8, 156.7, 147.5, 143.93, 143.88, 142.2, 142.13, 142.10, 141.9, 141.7, 141.44, 141.41, 141.34, 141.28, 141.25, 141.20, 141.17, 141.1, 141.02, 141.00, 139.4, 139.2, 138.7, 138.5, 138.3, 138.2, 137.8, 136.24, 136.19, 135.8, 135.7, 135.6, 135.4, 135.3, 134.41, 134.37, 134.36, 134.2, 134.0, 133.9, 133.0-132.9, 132.8-132.7, 132.6, 132.53, 132.47, 132.4-132.1, 130.94, 130.88, 130.7-130.6, 129.5, 129.3, 129.11-129.08, 128.1, 127.91-127.88, 127.82, 127.6-127.5, 126.8, 126.7, 126.6, 126.33-126.30, 121.7-121.5, 115.6, 115.5, 55.8, 51.0, the existence of at least two conformers causes the observation of signals of higher order; HRMS (ESI): [M⁺+4] calc.: 1203.09142 *m/z*, found: 1203.09206 *m/z*, Δ =0.53 ppm.

Compound 10: Under a nitrogen atmosphere tris(2,4,6-trichlorophenyl)methane (180 mg, 324 μ mol), Pd(MeCN)₂Cl₂ (3.0 mg, 13 μ mol), x-Phos (12 mg, 26 μ mol) and CuI (2 mg, 10 μ mol) were suspended in a quartz pressure vessel in (*i*-Pr)₂NH (2 ml) and degassed. A degassed solution of *N*,*N*-Di(4-methoxyphenyl)-*N*(4-(ethinyl)phenyl)amine (428 mg, 1.30 mmol) in absolute 1,4-dioxane (4 ml) was added and the reaction mixture stirred at 100 °C in a microwave oven for 1 h. After cooling, a degassed solution of *N*,*N*-Di(4-methoxyphenyl)-*N*(4-(ethinyl)phenyl)amine (321 mg, 972 μ mol) in absolute 1,4-dioxane (2 ml) was added stirred at 100 °C in a microwave oven for further 1 h. This procedure was repeated one more time. After cooling, EA (100 ml) was added and the mixture washed with a saturated NaCl solution (3 x 50 ml). The combined aqueous phases were extracted with EA (3 x 50 ml) and the combined organic phases dried over MgSO₄. The solvent was removed in vacuo and

the residue was purified by flash chromatography on silica gel DCM/petrol ether (1:1->2:1->3:1) and by gel permeation chromatography (CHCl₃). The pure compound **10** (160 mg, 110 μ mol, 34 %) was obtained as a yellow solid. M.p. 174 °C; ¹H NMR (600 MHz, acetone[d₆], 298 K): δ [ppm]=7.59 (3 H), 7.43 (3 H), 7.36 (AA', 6 H), 7.13 (AA', 12 H), 6.95 (BB', 12 H), 6.86 (s, 1 H), 6.77 (BB', 6 H), 3.80 (s, 18 H); ¹³C NMR (150.9 MHz, acetone[d₆], 298 K): δ [ppm]=157.9, 150.7, 140.4, 138.1, 137.3, 135.8, 133.5, 133.1, 131.4, 128.6, 126.2, 118.6, 115.8, 112.6, 94.4, 85.6, 55.7, 51.6; HRMS (ESI): [M⁺] calc.: 1429.26860 *m/z*, found: 1429.26884 *m/z*, Δ =0.17 ppm.



Temperature dependent NMR spectra of HAB-S, HAB-A and HAB-Model in acetone[d₆]



10



Fig. S4







Fig. S6





Fig. S7





Fig. S8













Fig. S11





Fig. S12









Fig. S14





Fig. S3-S15 ¹H and ¹³C NMR-spectra of **HAB-Model**, **HAB-A** and **HAB-S** in acetone[d6] measured at different temperatures.

Electrochemistry

Electrochemical measurements of the target compounds were performed to estimate the donor and acceptor redox potentials as well as interactions between these centres. The oxidation and reduction potentials were determined by CV and are given in Table S1 (see Fig. S16 for the CVs).

CV and square wave voltammetry (SWV) were performed with a GAMRY INSTRUMENTS potentiostat/galvanostat/ZRA model REFERENCE 600 workstation with a standard three electrode setup comprised of a platinum wire as counter electrode, an Ag/AgCl "leak free" reference electrode (Innovative Instruments, Inc. Tampa, USA) and a glass-sealed platinum wire of 1 mm diameter as working electrode. The measurements were done under an argon atmosphere in a flame-dried cell and referenced against the ferrocene/ferrocenium redox couple. DCM was dried over calcium hydride and distilled prior usage. The samples were measured at a concentration of $3 \cdot 10^{-4} - 7 \cdot 10^{-4}$ M. [Bu₄N][PF₆] was used as a supporting electrolyte and prepared according to a literature procedure.²⁹

Table S1Redox potentials form cyclic voltammograms of Star-Model, Star, HAB-Model, HAB-A andHAB-S ($\sim 3-7 \cdot 10^{-4}$ M) versus Fc/Fc⁺ in 0.2 M DCM/[Bu₄N][PF₆] at a scan rate of 250 mV s⁻¹

	Star-Model	Star	HAB-Model	HAB-A	HAB-S	
$E_{\rm red}/{ m mV}$	-960	-950	-1050	-1010, -1040, -1170	-1020, -1080, -1130	
$E_{\rm ox}/{ m mV}$	330	250, 320, 350	240	210, 260, 290	230, 280, 290	

^a multiple processes were fitted with DigiSim⁶.



Fig. S16 (a) CVs of **Star, Star-Model** in 0.2 M DCM/[Bu₄N][PF₆] measured at a scan rate of 250mV/s. (b) CVs of **HAB-S**, **HAB-A** and **HAB-Model** in 0.2 M DCM/[Bu₄N][PF₆] measured at a scan rate of 250mV/s. The second oxidation process of **HAB-Model** is attributed to the second oxidation of the TAA moiety.⁷

For a clearer representation of the electrochemical processes the square wave voltammetry (SWV) measurements are depicted in Fig. S17. The potentials determined by SWV agree with those of the CV measurements.



Fig. S17 (a) SWV of **Star** and **Star-Model** in 0.2 M DCM/[Bu₄N][PF₆] normalised to the signal maximum of the reduction. (b) SWV of **HAB-S**, **HAB-A** and **HAB-Model** in 0.2 M DCM/[Bu₄N][PF₆] normalised to the integral of the oxidation including the number of amine redox centres.

The oxidation processes at 210-350 mV are assigned to the first oxidation of the TAA centres. Typical values for TAAs are in the range of 250-400 mV^{2, 8} depending on the substitution pattern. Furthermore, the reduction signals at -950-(-1130) mV are typical of the PCTM units.9, 10 Both electrochemical processes were proved to be chemically fully reversible by thin-layer CV measurements and spectroelectrochemistry (SEC). The redox potentials of the model compounds HAB-Model and Star-Model have nearly the same potential difference of 1300 mV even though they are shifted by 100 mV to higher potentials in Star-Model. This reflects an equal free energy difference ΔG^{00} between ground and possible IV-CT states (see absorption section). The shift is most likely induced by the differing substitution pattern of the redox centres, which in case of Star-Model provides a more electron rich environment for both redox centres. In addition, their redox potentials are in good agreement with the potentials of their corresponding multi-chromophore compounds HAB-S, HAB-A and Star. In the latter multiple oxidation states from -3 to +3 can be reached according to the number of the redox centres present. However, the accessibility of oxidation states between -3 and +3 is limited as the redox processes show no distinct potential separation but a single broadened wave in the SWV. The potential separation in HAB-S, HAB-A and Star is indicative of electronic communication. Compared to HAB-Model with only one amine redox centre, the width at half-maximum of the oxidation signal is increased in HAB-S and to a greater extent in HAB-A, both containing three amine chromophores. In the multi-chromophore compounds, the width at half-maximum can be assessed by the difference of the two outermost potentials, increasing from 60 mV in HAB-S to 80 mV in HAB-A. The different potential splitting is correlated to the different substitution pattern of the HABs. Whereas in the symmetric HAB-S the amines are interconnected strictly by meta-substitution and separated by 1.2 nm (measured centre to centre from MM2 optimised^{11,12} structures), this is not the case in the asymmetric HAB. There, the centres are linked in meta-, para- and ortho-position with a minimum distance of 0.8 nm in the last case, resulting in a stronger electrostatic interaction upon oxidation, and, therefore, a larger potential separation. The same effects can be found in case of the reduction potentials albeit more pronounced. As redox potential splittings of multi-redoxchromophores are highly dependent on the solvent and supporting electrolyte,^{8, 13} their magnitude can differ in oxidation and reduction. The width at half-maximum of the SWV oxidation signal of **Star** is with 100 mV the largest compared to **HAB-S** and **HAB-A** although in **Star** the amines are separated by the largest distance (2.5 nm, measured centre to centre from MM2 optimised^{11,12} structures). We explain this by a better electronic communication between the redox centres.

Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) measurements were performed to characterise the PCTM centres in all radicals. Furthermore, the interactions between the three PCTM radical centres in **HAB-S** and **HAB-A** as well as between the TAA⁺⁻ and PCTM radical centres in the oxidised **HAB-Model** and **Star-Model** were investigated.

EPR measurements at X-band (9.8 GHz) were carried out at room temperature using a Bruker ELEXSYS E580 CW/FT EPR spectrometer. Typical experimental conditions for the acquisition of CW EPR spectra were as follows: 0.6 mW microwave power, 0.1 G field modulation, 100 kHz modulation frequency. Low temperature experiments were conducted in a liquid-flow He cryostat (Oxford ESR900) and a mercury iTC controller. The spectral simulations were performed using MATLAB 8.2 and the EasySpin 4.5.3 toolbox.³⁰









Fig. S18Simulated (red) and experimental (black) CW EPR spectra of a) HAB-Model, b) HAB-S and c)HAB-A in DCM at rt, 250 K and 230 K, respectively, and of d) Star-Model and e) Star in DCM at rt.

	g	$ a_{\rm N} /{ m mT}$	$ a_{\rm H} /{ m mT}$	$ a_{\rm C} /{ m mT}$
Star-Model	2.003	-	0.116 (4 H), 0.121 (2 H)	3.1, 1.31, 0.97
Star-Model ⁺⁻	-	-	-	-
Star	2.003	-	0.12 (6 H)	3.0, 1.3, 0.95
HAB-Model	2.003	-	0.12 (4 H), 0.13 (2 H)	3.1, 1.3, 1.0
HAB-Model ⁺⁻	2.003	~0.4	-	-
HAB-A	2.003	-	0.040 (12 H), 0.041 (6 H)	0.41, 0.35
HAB-S	2.003	-	0.041 (12 H), 0.042 (6 H)	0.42, 0.34

Table S2Electronic g factor and hyperfine coupling constants |a| from simulated EPR spectra of all radicalsin DCM^a

^a The EPR spectra of **HAB-S** and **HAB-A** were measured at 250 K and 230 K, respectively, those of **Star**, **Star-Model** and **HAB-Model** at rt. Radical cations were generated by oxidation with *tris*(bromophenyl)amminium hexachloroantimonate(V).

The EPR spectra were measured in DCM at rt with the exception of HAB-A and HAB-S which were measured at 230 K and 250 K, respectively, for a better hyperfine splitting resolution (see Fig. S18). The obtained spectra were simulated to obtain the electronic g-factor and the isotropic hyperfine coupling constants hfc |a| to nuclei with nonzero magnetic moments (see Table S2). For Star-Model, Star and HAB-Model EPR signals were observed which are characteristic for this type of PCTM, namely a g factor close to the value for the free electron $(g_{iso} = 2.003)$, and hfc to the *meta* hydrogen atoms of $|a_{\rm H}| = 0.12$ mT, to the α -carbon atom of $|a_{\rm C}| = 3.0$ mT and to neighbouring aromatic carbon atoms of $|a_c| = 1.29 \text{ mT}$ and $|a_c| = 1.05 \text{ mT}$.¹⁴ In agreement with the substitution pattern of the PCTM, the proton hfc of Star-Model and HAB-Model were found to be asymmetric showing two different hfc constants and that of Star to be symmetric with only one hfc constant. The signals of the multidimensional systems HAB-A and HAB-S are centred around the same characteristic g factor but all hfc constants are by a factor of ca. one third smaller. For multiradicals¹⁵⁻¹⁸ if each of the unpaired electrons has spin density on the other radical centres a hfc pattern results for all these radical centres with apparent hfc constants divided by the number of involved radical centres.^{19, 20} More precisely, this is observed when the electron exchange interaction J is much greater than the hfc constant |a| but the dipolar spin-spin interaction between the unpaired spins is weak. The same effect is found for the triradical compounds HAB-A and HAB-S. In these multiradicals the energy difference between states of differing spin multiplicity is negligible.

Both model compounds **HAB-Model** and **Star-Model** were oxidised to verify the necessity to consider diverse spin states regarding charge transfer. The EPR spectra of oxidised **HAB-Model** and **Star-Model** show basic differences (see Fig. S19).



Fig. S19 EPR spectra of oxidised (a) **Star-Model** and (b) **HAB-Model** by *tris*(bromophenyl)amminium hexachloroantimonate(V) at rt in DCM. **HAB-Model** was oxidised by ~35 % (green) and ~70 % (blue) maintaining the overall concentration of the radical centre. **Star-Model** was oxidised by 80 % (black) with the simulated signal in red.

Whereas the signal intensity of **Star-Model** gradually decreased upon stepwise oxidation, in case of **HAB-Model** a new broad signal is formed in addition to the characteristic PCTM signal. In principle, three possible scenarios have to be considered: 1) In biradicals, in which the two radical sites do not interact with each other, the electron exchange interaction constant J is smaller than the hfc constants |a| and thus only the spectra of the individual radical centres are observed. 2) If J is larger than |a| but smaller than the zero-field splitting parameter D the two centres are weakly interacting. In this case a "biradical" is observed with the typical changes to the hfc as explained above for the spectra of **HAB-A** and **HAB-S**. In the last case 3) J is considerably larger than D, meaning the two radical centres are strongly interacting. If so, singlet (EPR silent) and triplet states (only observable at low temperatures) are populated which differ in energy depending on the magnitude of J^{21} . In case of **HAB-Model** the characteristic PCTM signal is assigned to the remaining neutral radical species and the new broad signal belongs to the "biradical" = weak interacting case. The simulation indicated a g factor of 2.003 and although no hfc was directly observable due to the broadness of the signal a nitrogen hfc of ~0.41 mT was estimated. This hfc constant is roughly half the value of TAA^{+.} centres (~0.82 - 0.89 mT).^{22, 23} Following the explanation above J has to be much greater than the hfc constant |a| = 0.004 cm⁻¹ but has to be lower or to be in the range of D with typical values of |D| = 0.05-0.20 cm⁻¹²⁴ for biradical molecules.²¹ Regarding **Star-Model**, only a decrease of the PCTM signal is observed so that the formed cation has to be ESR silent. This implies a strong electron exchange interaction constant J and the formation of either a singlet or triplet species or both. To distinguish between these cases, EPR spectra were measured at 80 K but no change in the signal nor a half-field signal, typical of a triplet electronic state, could be observed. We therefore assume that Star-Model⁺ is in a singlet state, consistent with the antiferromagnetic coupling pathway between the radical centres.





Fig. S20 Least-squares fit (squares) of the reduced IV-CT band (line) of **Star** in DCM with parameters $\lambda_v = 1100 \text{ cm}^{-1}$, $\tilde{v}_v = 2030 \text{ cm}^{-1}$, $\lambda_o = 1960 \text{ cm}^{-1}$, and $\Delta G^{00} = 11360 \text{ cm}^{-1}$.

Spectroelectrochemistry

In order to investigate the spectral changes that undergo the radicals upon oxidation of the TAA moieties or reduction of the PCTM groups we performed spectroelectrochemistry experiments in DCM/electrolyte solution. The spectra of the oxidised and reduced species will also be helpful for the interpretation of transient absorption spectra.

Spectroelectrochemistry measurements were performed in a cylindrical quartz cell with a three electrode setup consisting of a platinum disc working electrode with a diameter of 6 mm, a gold-coated metal plate counter electrode and an Ag/AgCl pseudo reference electrode. The working electrode was positioned 100 µm above the quartz cell bottom by a µm-screw so that the adjusted thin-layer is completely electrolysed during the measurement. The voltage was applied by an EG & G Princeton Applied Research Model 283 potentiostat in steps of 20-100 mV. The UV/Vis/NIR spectra were measured with a JASCO V670 spectrometer. Here, the light beam was directed through the optically transparent bottom of the quartz cell and the thin-layer and reflected at the working electrode. The oxidation or reduction process was assumed to be finished when no further change in the spectrum was observed by varying the voltage. The extinction coefficients of the oxidised and reduced species were determined by comparison to the neutral starting compound.



Fig. S21 SEC of (a) the first oxidation and (b) the first reduction of **HAB-Model**. SEC of (c) the first oxidation and (d) the first reduction and **HAB-S**. The neutral species are given in blue, the fully electrolysed

species in brown. The applied potential was varied in 20 mV steps. The measurements were performed in a $DCM/[Bu_4N][PF_6]$ solution.

Radical **HAB-A** showed considerable irregularities in band intensity during the measurements possibly caused by deposition at the platinum working electrode rendering a discussion impossible. The spectroelectrochemistry of **HAB-Model** and **HAB-S** (Fig. S21) are very similar and will be discussed together. This is reasonable as the single electron redox steps in **HAB-S** are spectroscopically indiscernible. By reduction both compounds show the formation of an intensive absorption band at 18900-19300 cm⁻¹ which is attributed to π - π * transitions of the PCTM anion centre. These are expected at 20000 cm⁻¹ for a single PCTM¹⁴ but might be bathochromically shifted in mixed-valence compounds.² Furthermore, the radical centred transitions at 26600 cm⁻¹ as well the CT transitions at 15000-15600 cm⁻¹ decrease in intensity upon reduction.

During the oxidation process an intensive and narrow absorption band emerges at 13000-13100 cm⁻¹ with a shoulder at 15900-16100 cm⁻¹ characteristic for π - π * transitions in TAA radical cations.⁷ In addition, the absorption bands at 26600 cm⁻¹ are increasingly overlapped by a second transition which is also attributed to the TAA radical cation.⁷ In contrast, transitions localised at the neutral TAA centres in the range of 32500-33000 cm⁻¹ decrease. In the SEC of **HAB-S** one can clearly observe the appearance of a very weak absorption band at 8900 cm⁻¹. It is attributed to a charge transfer reversed from that of the neutral species, that is, from the PCTM radical to the electron poorer cationic TAA centre.² In **HAB-Model**⁺⁺ this band is not observed possibly due to an insufficient signal to noise ratio. The CT band in **HAB-S**⁺⁺ is very weak and that in **HAB-Model**⁺⁺ is expected to be one third as intensive.

By reducing **Star-Model**, the IV-CT absorption band (13500 cm⁻¹), band B (21500 cm⁻¹) and the bands between 24000 cm⁻¹ and 30000 cm⁻¹, all featuring transitions involving the radical centre (see Fig. S22), vanish. Furthermore, the reduced species shows a strong absorption band at 17600 cm⁻¹ with a shoulder band at 19900 cm⁻¹. These are caused by π - π * transitions at the anion centre.

During oxidation of **Star-Model** (see Fig. S22) the absorption bands at 26000 cm⁻¹ and 34500 cm⁻¹ decrease as expected for transitions located at the amine. Two intense absorption bands at 15400 cm⁻¹ and 13500 cm⁻¹ rise. The former asymmetric band is attributed to π - π * transitions of the radical cation, the latter is presumably a bridge-to-radical cation CT. This has been observed before in molecules in which an oxidised TAA is connected via a conjugated bridge to an acceptor.^{22, 25, 26} Even more interesting is an intense absorption band at 8100 cm⁻¹ (ε_{max} =32400 M⁻¹ cm⁻¹), attributed to a charge transfer from the PCTM radical to the TAA centre that is likewise present in the **HAB-S**.² The increased oscillator strength of this band in contrast to the IV-CT band in the neutral species is remarkable and cannot be explained by the bathochromic shift exclusively but must be caused by an increase in electronic coupling. For comparison, it is about five times as intensive as in **R2**.

Fig. S23 SEC of (a) the first oxidation and (b) the first reduction of **Star**. The neutral species is given in blue, the fully electrolysed species in brown. The applied potential was varied by 20 mV per step until no further change in the spectrum was observed. The measurements were performed in a DCM/[Bu₄N][PF₆] solution.

The reduction of **Star** (Fig. S23) induces spectral changes very similar to that of the model compound **Star-Model**. With the exception of the absorption bands D and E originating from π - π^* transitions located at the TAAs, all bands vanish including band A. As observed before, an intense absorption band originating from π - π^* transitions at the anion centre is forming at 16500 cm⁻¹. Its asymmetry is much less pronounced compared to that of **Star-Model**. This is most likely a result of the symmetric substitution pattern of the PCTM and thus a smaller splitting of the formally degenerate LUMO orbitals.

By oxidising **Star** (Fig. S23) to the trication we observed a continuous change of spectra. To get absorption spectra related to the individual oxidation steps the SEC data were factor-analysed by a global fitting routine implemented in the SpecFit software package (see Fig. S24).²⁷

Fig. S24 Global fit spectra of the SEC of **Star** in a DCM/[Bu_4N][PF_6] solution. The absorption spectra of the oxidation states are 0 (blue), +1 (green), +2 (orange) and +3 (red) are shown.

The quality of the fit was ascertained by comparison of the potential splitting calculated by the global fitting by CV. These values software to that measured are in good agreement (measured: $\Delta E_{\text{ox1-2}} = 70 \text{ mV}, \Delta E_{\text{ox2-3}} = 30 \text{ mV}, \text{ calculated: } \Delta E_{\text{ox1-2}} = 69 \text{ mV}, \Delta E_{\text{ox2-3}} = 38 \text{ mV}).$ However, it has to be stressed that the measured potential splitting for the three oxidation processes is very small (100 mV), so substantial deviations in the fitted absorption spectra arise by altering the splitting by a few millivolts. Nevertheless, several trends in the SEC spectra can be observed. Starting from the low energy part of the spectra, an intense absorption rises in Star⁺⁻ with a maximum at 6300 cm^{-1} , getting narrower and showing higher energetic maxima at 7400 cm^{-1} for **Star**²⁽⁺⁾ and at 8000 cm⁻¹ for $\mathbf{Star}^{3(+)}$. The absorption band of the trication is very similar to the low energy transition in the model compound Star-Model⁺⁻ and is likewise explained by a charge transfer from the radical centre to the oxidised TAA moieties. The illustrated changes in the SEC can be interpreted by the IV-CT transition depending on the oxidation state of the multidimensional chromophore. Due to oxidation of the second (in $Star^{2(+\cdot)}$) and third TAA centre (in Star³⁽⁺⁾) the electron donor ability of the central PCTM is reduced in comparison to Star⁺⁻ (see Table S3). This can be seen in the charge transfer parameters extracted by fitting the IV-CT absorptions bands of the cations by the Bixon-Jortner expression (eqn (4))(see Fig. S25).

Table S3Charge transfer parameters $\tilde{\nu}_v$, λ_o , λ_v and ΔG^{00} and transition dipole moments μ of the low energyIV-CT bands of Star⁺⁻, Star³⁽⁺⁻⁾ and Star-Model⁺⁻ in a DCM/[Bu₄N][PF₆] solution.

	μ / D	$\widetilde{\nu}_{\rm v}$ / cm ⁻¹	$\lambda_{\rm o}$ / cm ⁻¹	$\lambda_{\rm v}$ / cm ⁻¹	ΔG^{00} / cm ⁻¹
Star ⁺⁻	15.5	1770	3300	1230	1875
Star ^{2(+•)}	14.4	a	a	a	a
Star ^{3(+.)}	12.9	1470	2310	580	5140
Star-Model ⁺⁻	9.2	1400	2120	410	5710

^a could not be determined due to ambiguous fitting.

Fig. S25 Least-squares fits (squares) of the reduced IV-CT bands (line) of (a) \mathbf{Star}^{+} and (b) $\mathbf{Star}^{3(+)}$ in a DCM/[Bu₄N][PF₆] solution.

The free energy ΔG^{00} is substantially lower in **Star**⁺⁺ in comparison to **Star-Model**⁺⁺ indicating that the electron rich TAA moieties strengthen the donor ability of the radical centre in **Star**⁺⁺. At the same time both reorganization energies λ_v and λ_o are increased (see Table S3), whereas $\tilde{\nu}_v$ remains nearly unaltered. The IV-CT absorption band of **Star**²⁽⁺⁺⁾ obtained by SpecFit could not be fitted by the Bixon-Jortner expression as it is too symmetric to get reliable values for the parameters.²⁸ The obtained set of parameters for **Star**³⁽⁺⁺⁾ confirms the resemblance of its IV-CT bands to that of **Star-Model**⁺⁺ in spite of the different molecular structures.

Remarkably, the transition dipole moments (Table S3) of the IV-CT bands of \mathbf{Star}^{+} , $\mathbf{Star}^{2(+)}$ and $\mathbf{Star}^{3(+)}$ are slightly decreasing in this sequence. Although the number of possible charge transfer pathways increases equally with the oxidation state and thus an increase in band intensity is expected. In addition, the square of the transition dipole moment of the IV-CT band of $\mathbf{Star}^{3(+)}$ is about two times higher than that of \mathbf{Star} - \mathbf{Model}^{+} . A factor of three would be expected if the three possible CT pathways $\mathbf{Star}^{3(+)}$ are accounted for. Both phenomena can be attributed to a varying electronic environment of the IV-CT states in question with changing the redox centres either by altering substitution or oxidation of their substituents.

Fig. S26 Raw data of the fs-transient absorption corrected for chirp and scattered light of **HAB-Model** in DCM excited at 15200 cm⁻¹. The spectra are coloured from blue to red. The spectra are given in steps of around 25 fs (0.387-0.827 ps), 100 fs (0.827-2.013 ps) and 1 ps (2.013-15.093 ps).

Transient absorption

450

22000

Fig. S27 Raw data of the fs-transient absorption corrected for chirp and scattered light of HAB-A in DCM excited at 15200 cm⁻¹. The spectra are coloured from blue to red. The spectra are given in steps of around 25 fs (0.44-0.889 ps), 100 fs (0.889-2.018 ps) and 1 ps (2.018-17.107 ps).

Fig. S28 Raw data of the fs-transient absorption corrected for chirp and scattered light of **HAB-S** in DCM excited at 15200 cm⁻¹. The spectra are coloured from blue to red. The spectra are given in steps of around 25 fs (0.36-0.667 ps), 100 fs (0.693-2.027 ps) and 1 ps (2.027-15.093 ps).

Fig. S29 Raw data of the fs-transient absorption corrected for chirp and scattered light of **Star-Model** in DCM excited at 13800 cm⁻¹. The spectra are coloured from blue to red. The spectra are given in steps of around 25 fs (0.72-1.267 ps), 100 fs (1.267-2.256 ps) and 500 fs (2.256-10.227 ps).

ג/nm 500 750 700 650 600 550 450 400 0,06 0.907-2.02 ps 0.04 0,02 0,00 DOD -0,02 -0,04 -0,06 -0,08 16000 14000 18000 20000 22000 24000 vdcm⁻¹

Fig. S30 Raw data of the fs-transient absorption corrected for chirp and scattered light of **Star** in DCM excited at 13800 cm⁻¹. The spectra are coloured from blue to red. The spectra are given in steps of around 25 fs (0.313-0.893 ps), 100 fs (0.907-2.02 ps) and 500 fs (2.02-10.047 ps).

Fig. S31 (a) Raw data of the fs-transient absorption corrected for chirp and scattered light of **Star-Model** in DCM excited at 13800 cm^{-1} and (b) a sixth order polynomial fit to this data set in order to determine the band maxima. Data points around 12500 cm^{-1} (800 nm) were ignored for the fit because the spectra are in this range distorted by a measurement artefact from the fundamental amplifier output at 800 nm. The spectra are coloured

from blue to red. The spectra are given in steps of around 30 fs (0.8-1.2 ps, blue to cyan), 100 fs (1.2-1.707 ps, green to yellow) and 250 fs (1.707-4.92 ps, orange to red).

Transient absorption anisotropy measurements

In the case of **HAB-Model**, **HAB-A** and **HAB-S** the measured data differed from the defined ratio $I_{mag} = (I_{II}+2I_{\perp})/3$ by 2-6% and in the case of **Star-Model** and **Star** by 9-13%. This implies that the magic angle measurement has in each case too low intensity and/or the parallel and/or the perpendicular measurements have too high intensity by up to the mentioned values. We cannot ascertain if all or individual traces are inaccurate but the error is always in the same direction so that we assume it to be systematic. The origin is unknown as the pump intensity is stable (error of $\leq 1\%$). Furthermore, the polarisation of the pump was set by wire grids ensuring proper orientation. That was proven by complete extinction of the laser pulse due to perpendicular orientation of two wire grids. As a consequence the obtained anisotropy values can be inaccurate up to the same amount of error. However, the temporal evolution of the anisotropy should be unaffected and as we are assuming a systematic error in all the measurements the obtained data for the different compounds are comparable.

Fig. S32 The transient absorption traces (circles) I_{mag} (black), I_{II} (orange) and I_{\perp} (green) of **HAB-Model** pumped at 15200 cm⁻¹ and probed at 13000 cm⁻¹ (a), 13900 cm⁻¹ (b) and 19600 cm⁻¹ (c) in DCM and the respective

fits (lines) performed with a self written procedure based on MatLab (S36). All fit parameters are summarised in Tables S4 and S5.

Fig. S33 The transient absorption traces (circles) I_{mag} (black), I_{II} (orange) and I_{\perp} (green) of **HAB-A** pumped at 15200 cm⁻¹ and probed at 13000 cm⁻¹ (a), 13900 cm⁻¹ (b) and 19600 cm⁻¹ (c) in DCM and the respective fits (lines) performed with a self-written procedure based on MatLab (S36). All fit parameters are summarised in Tables S4 and S5.

Fig. S34 The transient absorption traces (circles) I_{mag} (black), I_{II} (orange) and I_{\perp} (green) of **HAB-S** pumped at 15200 cm⁻¹ and probed at 13000 cm⁻¹ (a), 13900 cm⁻¹ (b) and 19600 cm⁻¹ (c) in DCM and the respective fits (lines) performed with a self written procedure based on MatLab (S36). All fit parameters are summarised in Tables S4 and S5.

Fig. S35 The transient absorption traces (circles) I_{mag} (black), I_{II} (orange) and I_{\perp} (green) of **Star-Model** pumped at 13800 cm⁻¹ and probed at 13300 cm⁻¹ (a) and 14300 cm⁻¹ (b) in DCM and the respective fits (lines) performed with a self written procedure based on MatLab (S36). All fit parameters are summarised Tables S4 and S5.

Fig. S36 The transient biorption traces (circles) I_{mag} (black), I_{II} (orange) and I_{\perp} (green) of **Star** pumped at 13800 cm⁻¹ and probed at 13300 cm⁻¹ (a) and 14300 cm⁻¹ (b) in DCM and the respective fits (lines) performed with a self- written procedure based on MatLab (S36). All fit parameters are summarised in Tables S4 and S5.

Table S4	Isotropic	amplitudes	a and	decay	time	constants	au of	the	global	fits	of t	he	transient	absorption
traces I_{mag} , I_{II} and	nd I_{\perp} meas	ured for the	presen	ited con	mpou	nds at the g	given	proł	be wave	enum	nber	$\widetilde{v}_{\rm pro}$	obe in DC	М.

$\widetilde{v}_{\text{probe}}$ /cm ⁻¹		a_1	$ au_1$ /ps	a_2	$ au_2$ /ps	a_3	$ au_3$ /ps	a_4	$ au_4$ /ps	a_5	$ au_5$ /ps
13300	StarModel Star	-0.07 -0.38	0.59 0.02	0.09 -0.15	1.23 0.69	0.17	1.33				
14300	StarModel Star	-3.00 -4.19	0.88 1.03	3.00 4.12	0.90 1.06						
13000	HAB-Model	-0.17	0.01	240	0.01	-35.4	0.01	-0.02	1.12	0.03	3.27
	HAB-A	-0.17	0.01	240	0.02	-35.4	0.02	-0.04	0.98	0.09	4.21
	HAB-S	-0.17	0.01	240	0.01	-35.4	0.01	-0.04	1.01	0.08	4.08
13900	HAB-Model	2.45	0.04	-2.30	0.04	-0.02	1.02	0.04	3.28		
	HAB-A	0.01	0.01	-0.02	0.86	0.09	4.15				
	HAB-S	0.01	0.01	-0.01	1.01	0.06	4.00				
19600	HAB-Model	1.98	0.01	0.68	0.06	-0.03	0.91	0.05	3.34		
	HAB-A	0.02	0.02	-0.05	0.93	0.11	4.07				
	HAB-S	-0.02	0.16	0.5	0.76	-0.50	0.79	0.09	3.93		

$\widetilde{\nu}_{ ext{probe}}$		<i>a</i> .	$ au_1$	а.	$ au_2$	<i>a</i> .	$ au_3$
$/cm^{-1}$		u_1	/ps	u_2	/ps	u_3	/ps
13300	StarModel	0.22	0.97	0.12	100		
	Star	0.07	0.97	0.06	100		
14300	StarModel	0.16	0.12	0.24	100		
	Star	0.88	0.05	0.10	100		
13000	HAB-Model	0.26	0.13	0.06	0.90	-0.06	140
	HAB-A	0.22	0.10	0.04	0.91	-0.04	139
	HAB-S	0.12	0.18	0.03	1.04	-0.04	139
13900	HAB-Model	0.04	1.15	-0.06	101		
	HAB-A	0.04	1.38	-0.06	49.3		
	HAB-S	0.03	1.28	-0.05	49.3		
19600	HAB-Model	-0.04	0.39	0.001	100		
	HAB-A	0.002	100				
	HAB-S	-0.002	100				

Table S5Anisotropic amplitudes a and decay time constants τ of the global fits of the transient absorptiontraces I_{mag} , I_{II} and I_{\perp} measured for the presented compounds at the given probe wavenumber $\tilde{\nu}_{probe}$ in DCM.

Quantum chemical structure optimisations

Structure optimisations were performed with Gaussian09RevD.01.³¹ A global hybrid functional with an exact-exchange admixture of 30% and an SVP basis was used for all atoms.³² Solvent effects of DCM have been taken into account by a continuum solvent model (CPCM). The excitation energies, transition moments and excited state dipole moments were calculated by linear-response time-dependent density functional theory (TDDFT) using the same custom hybrids and SVP basis sets.

MATLAB script for global analysis

Matlab script used for the global analysis of the transient absorption traces I_{mag} , I_{II} and I_{\perp} .

```
function [x,resnorm,residual,exitflag,output] = FitA(n,b,xo,fucAx,fucAy)
options=optimset('Display','off','LargeScale','off','LevenbergMarquardt','on');
[x,resnorm,residual,exitflag,output] = lsqcurvefit(@nestedfun,xo,fucAx,fucAy,[],[],options);
                                                                                                                                                                                                                                                                                    function [Fo] =
nestedfun(x,fucAx)
l(1) = find(fucAx(:,1)>0,1,'last');
l(2) = find(fucAx(:,2)>0,1,'last');
l(3) = find(fucAx(:,3)>0,1,'last');
       fucMAx=fucAx(1:l(1),1);
       fucPx=fucAx(1:l(2),2);
       fucSx=fucAx(1:l(3),3);
       F{1,1}=zeros(max(1),3);
       m=1;
                                 while m \le n;
              IMA\{m\}=x(1,2*m+1)./2.*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1))./x(1,2*m+2)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1)).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x(1,1))).*exp(-(fucMAx-x
x(1,2).^{2./(2.*x(1,2*m+2)^{2})).*(1+erf((fucMAx-x(1,1)-x(1,2).^{2/(x(1,2*m+2))})./((2^{0.5}).*x(1,2))));
%#ok<AGROW>
                IP{m}=x(1,2*m+1)./2.*exp(-(fucPx-x(2,1))./x(1,2*m+2)).*exp(-
x(2,2).^2./(2.*x(1,2*m+2)^2)).*(1+erf((fucPx-x(2,1)-x(2,2).^2/(x(1,2*m+2)))./((2^{0.5}).*x(2,2))));
%#ok<AGROW>
                IS{m}=x(1,2*m+1)./2.*exp(-(fucSx-x(3,1))./x(1,2*m+2)).*exp(-
x(3,2).^{2./(2.*x(1,2*m+2)^{2})).*(1+erf((fucSx-x(3,1)-x(3,2).^{2/(x(1,2*m+2))})./((2^{0.5}).*x(3,2))));
%#ok<AGROW>
              F{1,1}(1:l(1),1)=F{1,1}(1:l(1),1)+IMA{1,m}(:,1);
```

```
F\{1,1\}(1:l(1),1)=F\{1,1\}(1:l(1),1)+HAF\{1,H\}(.,1)\}

F\{1,1\}(1:l(2),2)=F\{1,1\}(1:l(2),2)+IP\{1,M\}(.,1);

F\{1,1\}(1:l(3),3)=F\{1,1\}(1:l(3),3)+IS\{1,M\}(.,1);
```

a=1;

while $a \le b$;

```
\begin{split} &AS\{a+b^{*}(m-1)\}=&x(1,2^{*}m+1)^{*}x(1,2^{*}n+1+2^{*}a)./2.^{*}exp(-(fucSx-x(3,1))./(x(1,2^{*}m+2)^{*}x(1,2^{*}n+2+2^{*}a)/(x(1,2^{*}m+2)+x(1,2^{*}n+2+2^{*}a)))).^{*}exp(-x(3,2).^{2}./(2.^{*}(x(1,2^{*}m+2)^{*}x(1,2^{*}n+2+2^{*}a)/(x(1,2^{*}m+2)+x(1,2^{*}n+2+2^{*}a)))^{*}2)).^{*}(1+erf((fucSx-x(3,1)-x(3,2).^{2}/((x(1,2^{*}m+2)^{*}x(1,2^{*}n+2+2^{*}a)/(x(1,2^{*}m+2)+x(1,2^{*}n+2+2^{*}a)))))./((2^{*}0.5).^{*}x(3,2)))); \% \# ok < A GROW > 0
```

```
\begin{split} F\{1,1\}(1:l(2),2)=&F\{1,1\}(1:l(2),2)+2*AP\{1,a+b*(m-1)\}(:,1);\\ F\{1,1\}(1:l(3),3)=&F\{1,1\}(1:l(3),3)-AS\{1,a+b*(m-1)\}(:,1); \end{split}
```

a=a+1; end m=m+1;

end

Fo=cell2mat(F); Fo(:,2)=Fo(:,2).*x(2,2*n+3+2*b); Fo(:,3)=Fo(:,3).*x(3,2*n+3+2*b);

P(:,1)=Fo(:,2); S(:,1)=Fo(:,3);

End

% calculation of the anisotropy

```
u = round((x(2,1)-x(3,1))*1000);
```

fucPi(:,1)=(0:0.001:30); fucSi(:,1)=(0:0.001:30); fucAxi(:,1)=(0:0.001:30); fucAxi(:,2)=(0:0.001:30); fucAxi(:,3)=(0:0.001:30);

```
fucPi(:,2) = interp1(fucAx(1:l(2),2),fucAy(1:l(2),2),fucPi(:,1));
fucSi(:,2) = interp1(fucAx(1:l(3),3),fucAy(1:l(3),3),fucSi(:,1));
```

if u>=0

```
 \begin{array}{l} AniM=((fucPi(1+u:end,2)-fucSi(1:end-u,2))./(fucPi(1+u:end,2)+2*fucSi(1:end-u,2)));\\ else\\ AniM=((fucPi(1:end+u,2)-fucSi(1-u:end,2))./(fucPi(1:end+u,2)+2*fucSi(1-u:end,2)));\\ end \end{array}
```

fucFi=nestedfun(x,fucAxi);

```
if u>=0
AniF=((fucFi(1+u:end,2)-fucFi(1:end-u,3))./(fucFi(1+u:end,2)+2*fucFi(1:end-u,3)));
else
AniF=((fucFi(1:end+u,2)-fucFi(1-u:end,3))./(fucFi(1:end+u,2)+2*fucFi(1-u:end,3)));
end
```

ii=isnan(AniF); AniF(ii)=0;

% grafic Output

figure(1)

```
semilogx(fucAx(:,1),fucAy(:,1),'.k',fucAx(:,2),fucAy(:,2),'.b',fucAx(:,3),fucAy(:,3),'.g',fucAx,nestedfun(x,fucAx),'-
r')
title('Fit mit Exponentialfunktionen');
axis([0.5 10 0 0.03])
xlabel('t in ps');
ylabel('intensity a. u.');
legend('MA','P','S');
figure(2)
if u \ge 0
semilogx(fucPi(1+u:end,1),AniM(:,1),'.b',fucAxi(1+u:end,1),AniF(:,1),'-r')
else
semilogx(fucPi(1:end+u,1),AniM(:,1),'.b',fucAxi(1:end+u,1),AniF(:,1),'-r')
end
axis([0.5 10 -0.25 0.45])
xlabel('t in ps');
ylabel('anisotropy');
legend('Messdaten', 'FIT')
% save the data as ASCII
if u \ge 0
SAniso(:,1)=fucPi(1+u:end,1);
SAniso(:,2)=AniM(:,1);
SAniso(:,3)=AniF(:,1);
else
SAniso(:,1)=fucPi(1:end+u,1);
SAniso(:,2)=AniM(:,1);
SAniso(:,3)=AniF(:,1);
end
TFit=nestedfun(x,fucAx);
SFit(:,1)=fucAx(:,1);
SFit(:,2)=fucAy(:,1);
SFit(:,3)=TFit(:,1);
SFit(:,4)=fucAx(:,2);
SFit(:,5)=fucAy(:,2);
SFit(:,6)=TFit(:,2);
SFit(:,7)=fucAx(:,3);
SFit(:,8)=fucAy(:,3);
SFit(:,9)=TFit(:,3);
dlmwrite('Fit.txt',SFit,',')
dlmwrite('Anisotropie.txt',SAniso,',')
dlmwrite('xo.txt',x,',')
dlmwrite('fucAx.txt',fucAx,',')
dlmwrite('fucAy.txt',fucAy,',')
display(resnorm)
display(output)
display(u);
end
```

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