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Charge-Transfer Chromophores by Cycloaddition–Retro-electrocyclization: Multivalent Systems and Cascade Reactions[**]

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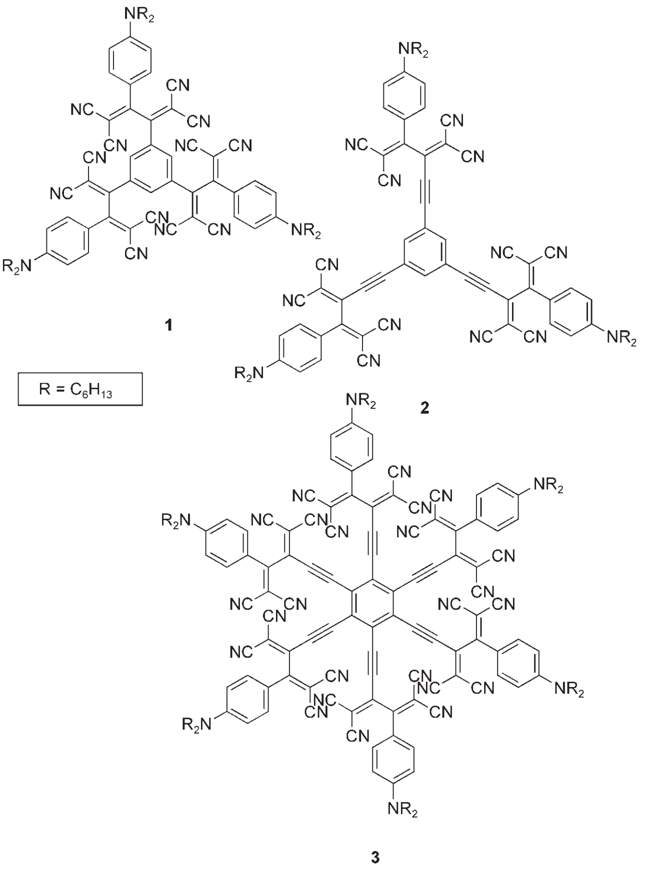
In memory of Yoshihiko Ito

Thermal [2+2] cycloadditions of tetracyanoethylene (TCNE) with electron-rich alkynes yield cyclobutenes, which in isolated cases have been shown to undergo retro-electrocyclization under formation of 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs).[1,2] Recently, we found that a wide variety of 4-*N*,*N*-dialkylanilino-substituted (DAA-substituted) alkynes react smoothly with TCNE to furnish DAA-donor-substituted TCBDs, often in quantitative yield. This new class of chromophores features intense intramolecular charge-transfer (CT) interactions with absorption maxima in the visible spectral range as well as promising third-order optical nonlinearities.[3]

A similar reaction occurs under the conditions of inverse electron demand. Hopf et al. showed that the strong electron donor tetrathiafulvalene (TTF) undergoes cycloaddition with electron-deficient acetylene moieties in cyanoethynylethenes, and the subsequent electrocyclic ring-opening afforded butadiene derivatives, 1,2-di(1,3-dithiol-2-ylidene)ethanes.[4] A similar reaction was observed by Hirsch and co-workers at the terminal acetylene moiety of α,ω-dicyanopolyynes.[5]

Here, we report the application of the reaction of TCNE with electron-rich alkynes to the high-yielding formation of dendrimer-type, multivalent charge-transfer chromophores that are capable of taking up an exceptional number of electrons under electrochemical conditions, thereby acting as a type of molecular batteries. Subsequently, we describe cascade reactions of polyyne oligomers, in which the cycloaddition/retro-electrocyclization with TCNE activates the adjacent C≡C bond electronically for the reaction with TTF and vice versa. This study culminates in a one-pot, eight-step domino reaction, with the formation of a single product resulting from four sequential cycloaddition/retro-electrocyclizations of TCNE and TTF molecules to give a octa-1,3,5,7-tetrayne.[6]

In our earlier work we showed that the fast addition of TCNE to DAA-substituted alkynes at room temperature had the character of a "click" reaction, thereby affording products in an atom-economic way with near quantitative yields.[3b] Thus, the tris-TCBD derivative **1**, which features an intramolecular CT band at 590 nm, was obtained from the corresponding triyne in 86% yield. The electrochemical properties of **1** are remarkable in that it undergoes six reversible one-electron reduction steps, each centered on a dicyanovinyl moiety, in the unprecedently narrow potential



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R = C_6H_{13}

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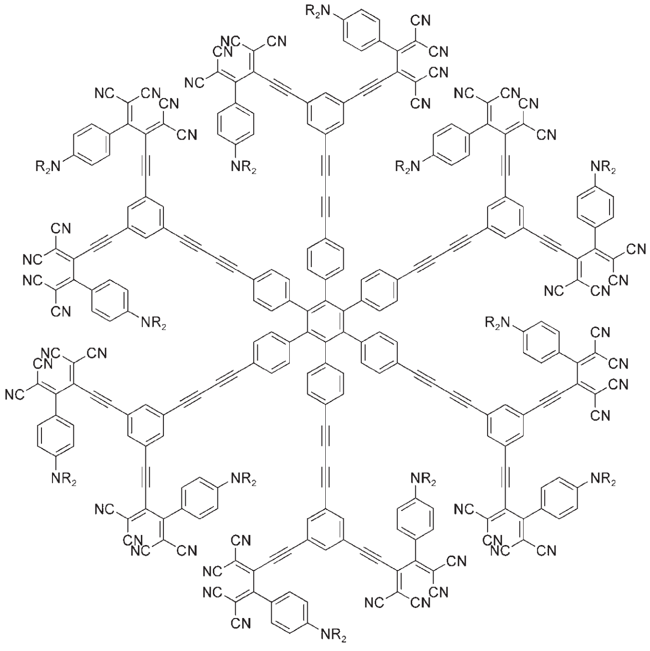
range between −0.69 and −1.69 V (versus the ferricinium/ferrocene couple, Fc^+/Fc) in CH_2Cl_2.[7] This finding initiated our search for larger multivalent CT systems that could act as powerful electron reservoirs.[8–11]

We prepared a large library of dendrimer-like DAA-substituted alkynes and report here on the new multivalent CT chromophores **2**–**4**.[12] In contrast to the tris-TCBD derivative **1**, buta-1,3-diyne-1,4-diyl rather than ethyne-1,2-diyl fragments were used to attach the DAA moieties to the central core to reduce the steric encumbrance and enhance the distance between pairs of dicyanovinyl acceptor moieties, thereby bringing the individual reduction potentials even closer.

The new multivalent TCBD derivatives **2**–**4** were obtained in excellent yields (77–96%) by the reaction of the corresponding alkyne precursors with TCNE in CH_2Cl_2 at 20 °C (see the Supporting Information). Thus, twelvefold addition of TCBD to produce **4** with the hexaphenylbenzene core proceeded in a rather spectacular 86% yield, which means nearly quantitative conversion in each of the twelve concurrent cycloaddition/retro-electrocyclization sequences (that is, 98% yield for each TCNE addition). All the compounds are stable at ambient temperature under air, and melt undecomposed above 100 °C. In agreement with our previous observation,[3b] each buta-1,3-diynyl moiety of the corresponding precursor reacted exclusively with one equivalent of TCNE at the more electron rich C≡C bond directly attached to the DAA substituent (even in the presence of an excess of TCNE at elevated temperature). The UV/Vis spectra of **2**–**4** are dominated by intense, broad CT bands accompanied by a long tail or shoulder reaching into the near infrared region. The absorption maxima and their intensities are rather indifferent to structural changes in the oligomeric TCBDs.



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Thus, the UV/Vis spectra of **2**–**4** in CH_2Cl_2 display CT bands at $\lambda_{max} = 460$ nm (2.70 eV, $\varepsilon = 114\,300\,\text{M}^{-1}\text{cm}^{-1}$), $\lambda_{max} = 476$ nm (2.60 eV, $\varepsilon = 110\,000\,\text{M}^{-1}\text{cm}^{-1}$), and $\lambda_{max} = 456$ nm (2.72 eV, $\varepsilon = 91\,400\,\text{M}^{-1}\text{cm}^{-1}$), respectively (see the Supporting Information).

The redox properties of **2**–**4** as well as their precursors (see the Supporting Information) were studied by cyclic voltammetry (CV) and rotating-disc voltammetry (RDV) in CH_2Cl_2 (+0.1 M nBu$_4$NPF$_6$). Thus, the oxidation of all the DAA moieties in **2**–**4** occurs in a single, reversible multielectron transfer. As an example, dendrimer **4** is oxidized in a unique 12-electron transfer step at +0.89 V (versus Fc^+/Fc). Hence, all the DAA moieties in a multivalent system behave as independent redox centers (Table 1).[11a] Such a behavior has been observed previously in the case of ferrocenyl dendrimers by Astruc and co-workers[11b,c] and others.[11d]

Table 1: Electrochemical data of CT chromophores **2**–**5** observed by CV and RDV in CH_2Cl_2 (+0.1 M nBu$_4$NPF$_6$).[a]

	CV			RDV	
	$E°$ [V][b]	ΔE_p [mV][c]	E_p [V][d]	$E_{1/2}$ [V][e]	slope [mV][f]
2	+0.88	90		+0.87 (3e⁻)	60
	−0.67	160		−0.73 (3e⁻)	120
	−1.13	180		−1.28 (3e⁻)	150
3	+0.89	100		+0.90 (6e⁻)	85
	−0.46	60			
	−0.60	60			
	−0.70	60		−0.80 (6e⁻)	400
	−0.76	60			
	−0.95	60			
	−1.07	60			
	−1.57	150		−1.55 (6e⁻)	200
4	+0.87	50		+0.89 (12e⁻)	50
	−0.70	100		−0.73 (12e⁻)[g]	130
	−1.10	220			
5	+0.95	100		+0.96 (3e⁻)	70
			+0.80	+0.81 (2e⁻)	70
	+0.61	115		+0.65 (2e⁻)	60
	+0.40	110		+0.41 (2e⁻)	70
	−1.12				
	−1.22			−1.40	300
	−1.35				
	−1.40				
	−1.48				
	−1.55				

[a] All potentials are given versus the Fc^+/Fc couple used as internal standard.The electrochemical data for all other compounds reported in this paper can be found in the Supporting Information. [b] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_p = E_{ox} - E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [d] E_p = Irreversible peak potential. [e] $E_{1/2}$ = Half-wave potential. [f] Slope of the linearized plot of E versus $\log[I/(I_{lim} - I)]$, where I_{lim} is the limiting current and I the current. [g] Unresolved spread-out wave.

Compounds **2**–**4** undergo several reversible one-electron reduction steps centered on the dicyanovinyl units: each TCBD moiety can accommodate two electrons (Table 1). Thus, **3** with six TCBD moieties shows six well-separated one-electron reduction steps (from −0.46 V to −1.07 V) followed by an unresolved six-electron transfer at −1.57 V. It can be

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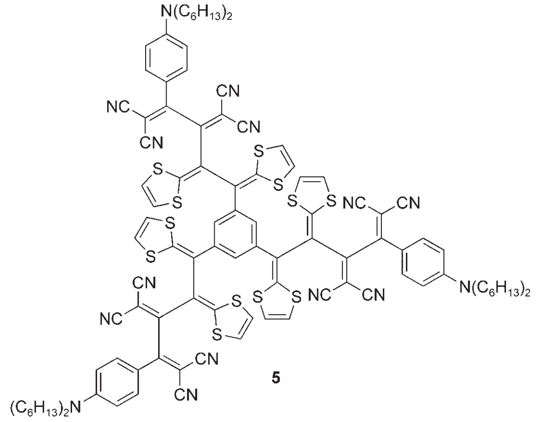
assumed that the first six one-electron transfers are centered on dicyanovinyl moieties of different TCBD moieties. Dendrimer **4** accepts 24 electrons in two reversible 12-electron reduction steps at −0.70 V and −1.10 V, respectively (for the CV traces, see the Supporting Information). The reversible injection of 24 electrons into a molecule within a narrow potential range between −0.70 V and −1.10 V is quite remarkable, also in terms of the solubility of the highly charged species formed. The differences in peak potentials for the first and second reduction step are 100 mV and 220 mV, respectively. The peak potentials are scan-rate independent up to 1 V$\,$s^{-1}. These characteristics are typical for unresolved overlapping electron transfers occurring at slightly different potentials, which denotes very little interaction between the different TCBD groups in **4**.[11a]

While exploring the reactivity of the tris-TCBD derivative **2**, we found the C≡C bonds adjacent to the electron-accepting TCBD units to be sufficiently electron-deficient and, hence, activated for the [2+2] cycloaddition to TTF, as previously observed by Hopf and co-workers and Hirsch and co-workers for cyanoethynylethenes and α,ω-dicyanopolyynes, respectively.[4,5] Upon heating in MeCN, **2** undergoes threefold [2+2] cycloaddition to TTF followed by retro-electrocyclization to give adduct **5** in 47 % yield (that is, 78 % yield for each TTF addition). The proposed constitution of this black-metallic solid, which melts at 214–217 °C, was unambiguously proven by the spectral data (see the Supporting Information), although complex conformational equilibria complicate the interpretation of the ^{1}H and ^{13}C NMR spectra. Highly reproducible voltammograms were measured which showed three successive reversible two-electron oxidation steps of the three 1,2-di(1,3-dithiol-2-ylidene)ethane moieties at +0.41, +0.65, and +0.81 V in addition to a three-electron oxidation at +0.96 V of the three DAA moieties and six individual reduction waves between −1.12 V and −1.55 V for the six dicyanovinyl units. The UV/Vis spectrum of **5** in CH_2Cl_2 is dominated by an intense broad CT band at $\lambda_{max} = 482$ nm (2.57 eV, $\varepsilon = 132\,000\,M^{-1}\,cm^{-1}$; see the Supporting Information).



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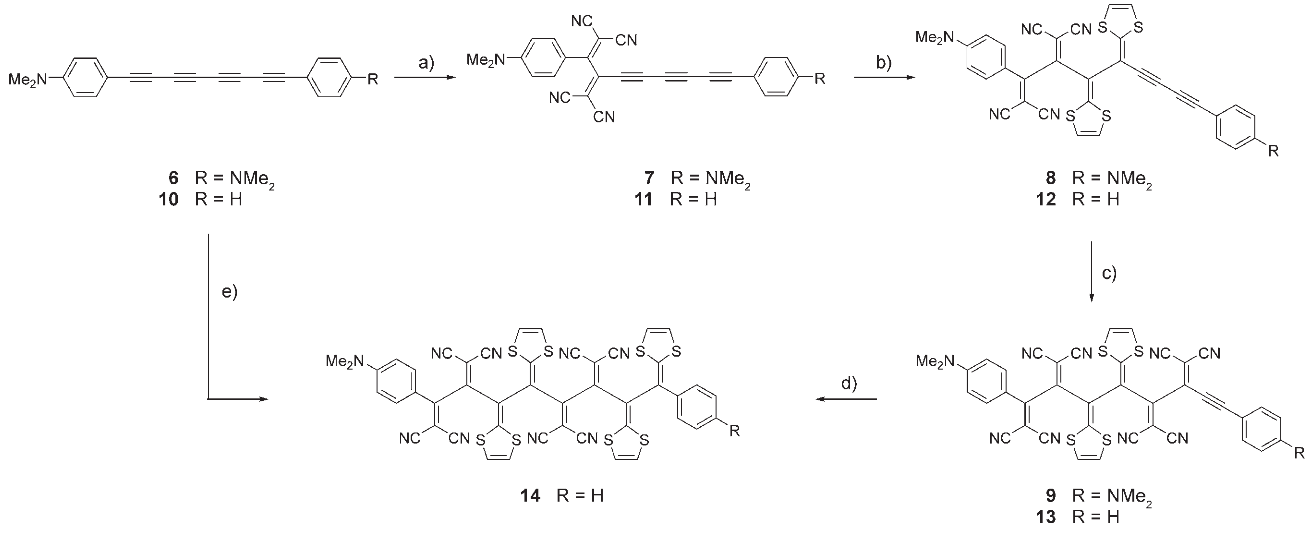
Building on this result, we decided to construct rodlike oligomeric donor–acceptor (D-A) systems where the donor part consists of 1,2-di(1,3-dithiol-2-ylidene)ethane units, while the 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) framework serves as the acceptor. A cascade of successive TCNE/TTF additions to end-capped polyynes, controlled by the electronic properties of the reacting C≡C bonds, would provide access to a new class of conjugated [AB]-type oligomers and polymers[13] with dendralene-type backbones.[14]

Thus, bis-DAA-substituted tetrayne **6** (see the Supporting Information) was treated with one equivalent of TCNE in CH_2Cl_2 to yield TCBD **7** (72 %; for the X-ray structure, see the Supporting Information) which reacted subsequently with an excess of TTF in MeCN to afford the hybrid TCNE-TTF adduct **8** in 80 % yield (Scheme 1). In the next step, derivative **8** gave A-D-A system **9** (83 %) upon reaction with TCNE (Scheme 1). The regioselectivity of the TCNE addition is determined by the stronger 1,2-di(1,3-dithiol-2-ylidene)ethane donor. However, the attempted cycloaddition of the



Scheme 1. Cascade of alternating [2+2] cycloadditions/retro-electrocyclizations of TCNE/TTF to octatetraynes **6** and **10**. a) TCNE, CH_2Cl_2, 10–14 h, 20 °C, 72 % (**7**), 95 % (**11**). b) TTF, MeCN, 16–17 h, 60 °C, 80 % (**8**), 78 % (**12**). c) TCNE, CH_2Cl_2, 14–22 h, 20 °C, 83 % (**9**), 92 % (**13**). d) TTF, CH_2Cl_2/MeCN 1:1, 3 h, 50 °C, 21 % (**14**). e) TCNE, TTF, CH_2Cl_2/MeCN 1:1, 22 h, 50 °C, 21 % (**14**).

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remaining acetylenic bond in **9** to TTF failed. This triple bond is not sufficiently electron deficient to undergo [2+2] cycloaddition to TTF.

To eliminate this "electronic confusion" of the last triple bond, we started from mono-DAA-, monophenyl-substituted tetrayne **10** (see the Supporting Information). The TCBD derivative **11** was formed in nearly quantitive yield (95%) using one equivalent of TCNE, and subsequent reaction with TTF afforded adduct **12** (78%; Scheme 1). Treatment of A-D chromophore **12** with TCNE gave A-D-A derivative **13** in nearly quantitative yield (92%). Finally, the C≡C bond in **13**, which is now electron deficient and no longer "electronically confused", was subjected to the reaction with an excess of TTF to yield the A-D-A-D chromophore **14** as a black-metallic solid (m.p. 260°C) in 21% yield (Scheme 1). The reduced yield of **14** is presumably caused by steric crowding around the reacting C≡C bond.

We next attempted the cascade of successive [2+2] TCNE/TTF additions to the end-capped tetrayne **10** in a one-pot setup. Mixing **10** with an excess of TCNE and TTF in MeCN/CH_2Cl_2 at 50°C indeed yielded the [ABAB] system **14** in 21% yield, which corresponds to a yield of 68% per cycloaddition/retro-electrocyclization step (Scheme 1).

As in the case of **5**, the NMR characterization of the hybrid TTF-TCNE chromophores **8**, **9**, and **12**–**14** was seriously complicated by the presence of complex conformational equilibria in solution.[15] The UV/Vis spectra of **8**, **9**, and **12**–**14** are dominated by intense, broad CT bands with absorption maxima λ_{max} between 460 and 480 nm (see the Supporting Information).

While the redox properties of all the D-A chromophores have already been studied by CV and RDV (for a listing and discussion of the data for **6**–**14**, see the Supporting Information), the spin properties of the polyanions and polycations with odd numbers of electrons by electron paramagnetic resonance (EPR) are currently under investigation. Furthermore, the exploration of second- and third-order optical nonlinearities and other advanced materials properties of the fascinating new charge-transfer chromophores reported in this manuscript is now intensively being pursued.

In summary, we have demonstrated the enormous synthetic potential and complementarity of the [2+2] cycloadditions of TCNE and TTF to alkynes for the construction of multivalent charge-transfer chromophores. A one-pot protocol for electronically controlled cascade TCNE/TTF additions to polyynes opens up an easy access to a new family of conjugated [AB]-type oligomers and polymers, and application to longer polyynes is now under investigation.

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[1] To the best of our knowledge, this cascade transformation was first reported for the reaction of acrylonitriles with *N*,*N*-diethylaminoprop-1-yne, see J. Ficini, A. M. Touzin, *Bull. Soc. Chim. Fr.* **1972**, *6*, 2385–2387; for an early reference to the addition of TCNE, see: M. I. Bruce, J. R. Rodgers, M. R. Snow, A. G. Swincer, *J. Chem. Soc. Chem. Commun.* **1981**, 271–272.

[2] For some more recent work, see a) C. Cai, I. Liakatas, M.-S. Wong, M. Bösch, C. Bosshard, P. Günter, S. Concilio, N. Tirelli, U. W. Suter, *Org. Lett.* **1999**, *1*, 1847–1849; b) K. Onitsuka, N. Ose, F. Ozawa, S. Takahashi, *J. Organomet. Chem.* **1999**, *578*, 169–177; c) T. Mochida, S. Yamazaki, *J. Chem. Soc. Dalton Trans.* **2002**, 3559–3564; d) Y. Morioka, N. Yoshizawa, J.-i. Nishida, Y. Yamashita, *Chem. Lett.* **2004**, *33*, 1190–1191.

[3] a) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* **2005**, 737–739; b) T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889–1905.

[4] H. Hopf, M. Kreutzer, P. G. Jones, *Angew. Chem.* **1991**, *103*, 1148–1149; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1127–1128.

[5] G. Schermann, O. Vostrowsky, A. Hirsch, *Eur. J. Org. Chem.* **1999**, 2491–2500.

[6] For cascade and domino reactions, see: L. F. Tietze, G. Brasche, K. Gericke, *Domino Reactions in Organic Synthesis*, Wiley-VCH, Weinheim, **2006**.

[7] Note that the six reduction steps of fullerene C_{60} in MeCN/toluene occur within a much wider potential range between −0.98 and −3.26 V versus Fc^+/Fc: Q. Xie, E. Pérez-Cordero, L. Echegoyen, *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980.

[8] a) D. Astruc, *Acc. Chem. Res.* **1986**, *19*, 377–383; b) D. Astruc, *Acc. Chem. Res.* **2000**, *33*, 287–298; c) J. Ruiz, C. Pradet, F. Varret, D. Astruc, *Chem. Commun.* **2002**, 1108–1109.

[9] D. Bonifazi, M. Scholl, F. Song, L. Echegoyen, G. Accorsi, N. Armaroli, F. Diederich, *Angew. Chem.* **2003**, *115*, 5116–5120; *Angew. Chem. Int. Ed.* **2003**, *42*, 4966–4970.

[10] R. Schenk, H. Gregorius, K. Meerholz, J. Heinze, K. Müllen, *J. Am. Chem. Soc.* **1991**, *113*, 2634–2647.

[11] a) J. B. Flanagan, S. Margel, A. J. Bard, F. C. Anson, *J. Am. Chem. Soc.* **1978**, *100*, 4248–4253; b) C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **1997**, *119*, 2588–2589; c) M.-C. Daniel, J. Ruiz, J.-C. Blais, N. Daro, D. Astruc, *Chem. Eur. J.* **2003**, *9*, 4371–4379; d) V. J. Chebny, D. Dhar, S. V. Lindeman, R. Rathore, *Org. Lett.* **2006**, *8*, 5041–5044; e) K. Hosomizu, H. Imahori, U. Hahn, J.-F. Nierengarten, A. Listorti, N. Armaroli, T. Nemoto, S. Isoda, *J. Phys. Chem. C* **2007**, *111*, 2777–2786.

[12] All new compounds were fully characterized by m.p., IR, UV/Vis, ^1H and ^{13}C NMR spectroscopy as well as HR-MALDI-MS and/or elemental analysis; for full experimental details, see the Supporting Information. An account of the entire multivalent CT compound library will be published as a full paper.

[13] a) Q. T. Zhang, J. M. Tour, *J. Am. Chem. Soc.* **1997**, *119*, 5065–5066; b) Q. T. Zhang, J. M. Tour, *J. Am. Chem. Soc.* **1998**, *120*, 5355–5362; c) C. A. Thomas, K. Zong, K. A. Abboud, P. J. Steel, J. R. Reynolds, *J. Am. Chem. Soc.* **2004**, *126*, 16440–16450.

[14] a) H. Hopf, *Angew. Chem.* **1984**, *96*, 947–958; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 948–959; b) H. Hopf, *Angew. Chem.* **2001**, *113*, 727–729; *Angew. Chem. Int. Ed.* **2001**, *40*, 705–707.

[15] The limited stability of chromophores **5**, **8**, **9**, and **12**–**14** at high temperatures together with their poor solubility at low temperatures reduced the available temperature range for VT-NMR experiments (253–353 K). Thus, only the ^1H NMR spectra of derivatives **8** and **12** could be recorded beyond the coalescence temperature of all signals. The temperature at which frozen conformations could be observed by ^1H NMR spectroscopy was not reached because of the low solubility of the compounds. Coalescence of the ^{13}C NMR signals was not observed within the available temperature range. Thus, complex ^{13}C NMR spectra of **5**, **8**, **9** and **12**–**14** are reported in the Supporting Information as empiric enumeration of observed signals.

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