DOI: 10.1002/anie.201307756

Noncovalent Interactions

Supramolecular Assemblies by Charge-Transfer Interactions between Donor and Acceptor Chromophores

*Anindita Das and Suhrit Ghosh**

amphiphiles · charge transfer · gels · liquid crystals · supramolecular chemistry

We have collated various supramolecular designs that utilize organic donor–acceptor CT complexation to generate noncovalently co-assembled structures including fibrillar gels, micelles, vesicles, nanotubes, foldamers, conformationally restricted macromolecules, and liquid crystalline phases. Possibly inspired by nature, chemists have extensively used hydrogen bonding as a tool for supramolecular assemblies of a diverse range of abiotic building blocks. As a structural motif, CT complexes can be compared to hydrogen-bonded complexes in its directional nature and complementarities. Additional advantages of CT interactions include wider solvent tolerance and easy spectroscopic probing. Nevertheless the major limitation is their low association constant. This article shows different strategies have evolved over the years to overcome this drawback by reinforcing the CT interactions with auxiliary noncovalent forces without hampering the alternate stacking mode. Emerging reports on promising CT complexes in organic electronics are intimately related to various supramolecular designs that one can postulate based on donor–acceptor CT interactions.

1. Introduction

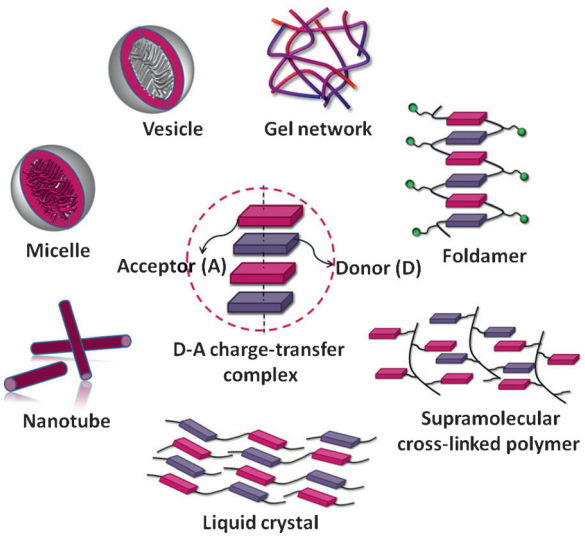
Supramolecular chemistry[1–3] has created an opportunity for science practitioners from various disciplines to assemble under a common platform and explore the enormous diversity in the organization of molecules through noncovalent interactions, spanning length scales ranging from nanometers to several micrometers. Various subareas of this rather diverse research field that include self-assembled π-conjugated chromophores,[4–10] supramolecular polymers,[11–12] crystal engineering,[13] conceptual development of the supramolecular synthon,[14] self-organization of metal-containing building blocks,[15,16] assembly of π-conjugated amphiphiles[17] and peptides[18] in aqueous medium, supramolecular materials,[19,20] fibrillar gels,[21] and the relevance of supramolecular chemistry in biology,[22] have been extensively reviewed in the recent past. It is evident that over the past several years, incredible progress has been made in terms of identifying suitable molecular entities with specific recognition units for directional interactions and understanding structural nuances of the building blocks which govern the molecular-level interactions and consequently the macroscopic properties.

Hydrogen bonding has been most extensively studied in this context owing to its highly directional nature, structural diversity, and moderate to very high association constants. Numerous examples on hydrogen-bonding-promoted, well-defined supramolecular assemblies have been discussed in several review articles concerning the pros and cons of the noncovalent synthesis using hydrogen bonds,[23] quadruple hydrogen-bonded systems,[24] methods for modulating the strength of hydrogen bonds,[25] supramolecular polymers,[11] and self-assembled π-conjugated chromophores.[26] It involves a donor and an acceptor unit containing an acidic hydrogen atom and a nonbonding electron lone pair, respectively. Depending on whether they are part of a single molecule or different molecules, the sequence of connectivity, as well as other parameters, hydrogen bonding can be either self-complementary (amide, urea, carboxylic acid, urethane, urido

[*] A. Das, Dr. S. Ghosh
Polymer Science Unit
Indian Association for the Cultivation of Science
2A & 2B Raja S. C. Mullick Road, Kolkata, 700032 (India)
E-mail: psusg2@iacs.res.in

pyrimidine) or two units can be complementary to each other (hydrogen bonding between two different nucleobases).

Charge-transfer (CT) interactions drive the alternate stacking of aromatic donor (D) and acceptor (A) chromophores[27] and is comparable to hydrogen bonding because of its inherent complementary nature in alternating placement of the D and A units. CT complexes of various D–A pairs have been studied for a long time.[28–33] D–A cocrystals were isolated years ago[34,35] and are sometimes called CT salts.[36–38] Nevertheless, there are fewer examples of such CT complexes when compared to those of hydrogen-bonding-driven self-organized systems. Possibly, very low to moderate association constants, particularly in case of intermolecular D–A complexes, limit their potential in the creation of the organized structures with long-range order. Thus reinforcing CT complexes by using other noncovalent forces such as solvophobic forces, metal–ligand coordination, hydrogen bonding, etc., has been used as common design strategies to construct stable supramolecular structures. Examples related to co-assemblies driven by CT complexation have been partly discussed in a few review articles which are primarily concerned with aromatic interactions,[39–40] foldamers,[41] gels,[42] and organic electronics.[43] Nevertheless significant new results have been published recently on complexation promoted by D–A interactions for a diverse range of supramolecular assemblies such as organogels, synthetic ion channels, rotaxanes, catenanes, foldamers, superamphiphiles, and liquid crystalline materials. In this review, we have brought together such examples of supramolecular structures (Scheme 1) having ground-state CT interactions as the central theme, and highlight the scope of this classical nonbonding interaction as a structural motif for efficient co-assembly of building blocks containing electron-rich and deficient chromophores. Although CT complexes have been extensively used to produce many fascinating interlocked compounds such as rotaxanes and catenanes, they have been excluded from this article as they are reviewed elsewhere.[44–48] External host-stabilized (such as cucurbit-[8]-uril) CT complexes and related supramolecular assemblies have also been reviewed recently[49] and thus are not part of the present article.



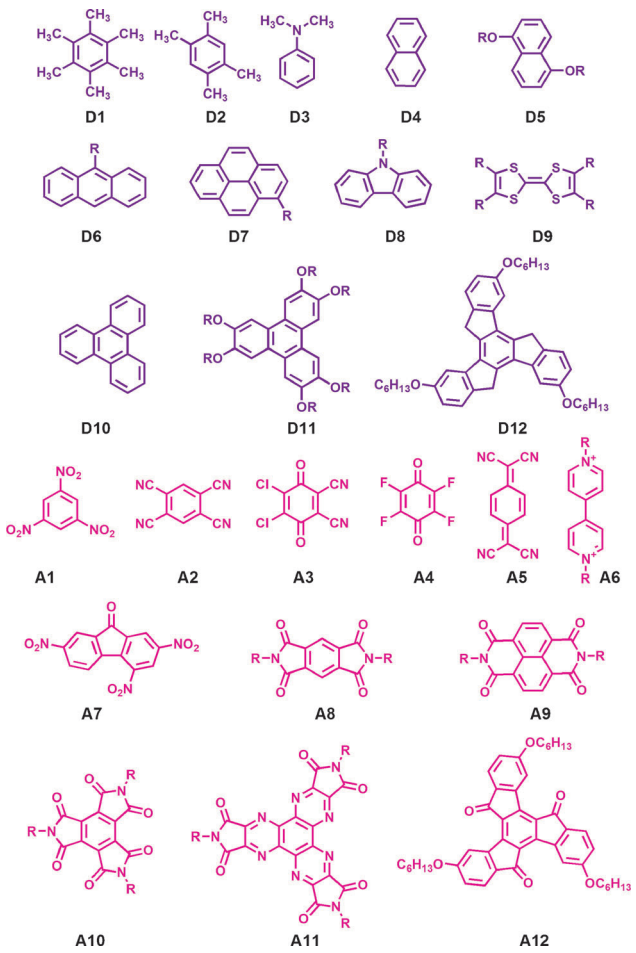
Scheme 1. Different kinds of D-A supramolecular assemblies discussed in this Minireview.

2. D and A Chromophores and CT Complexes

Description of D and A chromophores: Over the last 50 years several donor and acceptor chromophores have been examined in the context of their propensity to form CT complexes. The large number of molecules published so far makes it practically impossible to provide a comprehensive account on their structures and properties in this subsection. Thus we have chosen a few selected examples of representative π donors (D1–D12) and acceptors (A1–A12) (Scheme 2) to highlight important aspects of CT complexes. It is also important to note that this list does not include either lone-pair (n) donors such as aliphatic amines, phosphines, and alcohols, or σ acceptors such as I_2, Br_2, and ICN[27] because this article is concerned with π donors and acceptors. Hexamethylbenzene (D1), tetramethylbenzene (D2), *N*,*N*-dimethylaniline (D3), and many other structurally related benzene derivatives substituted with electron-donating groups were identified as donor units early on.[27] Likewise 1,3,5-trinitrobenzene (A1), tetracyanobenzene (A2), and structurally similar chromophores with electron-withdrawing

Anindita Das received an M. Sc. (Organic Chemistry) from the University of Calcutta, India in 2009 and joined the Indian Association for the Cultivation of Science, Kolkata, India for a PhD. Since then she has been working in the area of supramolecular assembly of donor–acceptor chromophores and amphiphilic macromolecules.

Suhrit Ghosh completed an M. S. (Chemistry) at the Indian Institute of Science, Bangalore in 2000 and subsequently obtained a Ph.D. in 2006 on folded polymers. He conducted postdoctoral studies at the University of Massachusetts, Amherst, and at the University of Würzburg. In 2008 he joined the Polymer Science Unit at the Indian Association for the Cultivation of Science, Kolkata, where he currently holds the position of an Associate Professor. His research interests include supramolecular assembly of π-conjugated chromophores, aggregation of amphiphilic polymers, and their interaction with bio-macromolecules.



Scheme 2. Structures of representative π-donors and acceptors.

groups act as acceptor counterparts to form CT complexes. Several quinone derivatives such as 2,3-dichloro-5,6-dicyano *p*-benzoquinone (A3), tetrafluoro-*p*-benzoquinone (A4), and other related compounds have been also extensively studied as acceptor units for CT interactions with benzene-ring-containing donors.[27] Derivatives of aromatic compounds with larger π surfaces, such as naphthalene (D4), dialkoxynaphthalene (D5), anthracene (D6), pyrene (D7), carbazole (D8), and triphenylene (D10) can act as donor components in the formation of CT complexes with acceptors such as 2,4,7-trinitrofluorenone (A7), pyromellitic diimide (A8), naphthalene-diimide (A9), mellitic triimide (A10), and viologen (A6) derivatives. Different combinations of these D–A pairs have found widespread interest in the construction of a diverse range of supramolecular assemblies which are discussed in the subsequent sections of this article. Tetrathiafulvalene (TTF) and its derivatives[50] (D9) represent an important class of donors which can form efficient CT complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, A5), having metallic behavior,[51] and also with A6, A8, and A9 for formation of interlocked compounds such as rotaxanes and catenanes.[44–48] A few recent examples suggest that C_3-symmetric donors such as D11 (hexakisalkoxytriphenylene) and D12 (truxene derivatives) can form highly stable D–A pairs with the complementary acceptors A11 (hexaazatriphenylene)[52] and A12 (truxenone derivatives),[53] respectively, owing to their almost identical shape and size.

Probing CT complexes: According to molecular orbital treatments, the CT band arises as a result of an electronic transition from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor. Formation of a CT complex can be readily detected by the appearance of a new single or multiple low-energy absorption bands while significantly retaining the absorption peaks of the individual D and A components. However as the extinction coefficients of the broad CT bands are not so high in many examples, it becomes difficult to identify them in a dilute solution of a 1:1 D/A mixture for weak complexes. Thus increasing the concentration of one of the components often helps in visualizing the CT band. In many examples, CT complexes also show a new emission band having a mirror image relationship with the CT absorption spectra.[27] They are also routinely probed by NMR techniques[54] in which face-to-face alternate D–A stacking results in upfield shifts of the aromatic protons because of the shielding effect. Additionally, two-dimensional (2D) NMR spectroscopic tools have been used in the recent past[54] to detect spatial communication among the protons from the alternately stacked D and A units. Recently electronic structures of D–A assemblies have been studied by ultraviolet photoelectron spectroscopy.[55]

Association constant: Binding affinities of D–A complexes depend on several parameters, including the donating and accepting ability of the D and A chromophores, respectively, steric crowding imparted by the substituent on the aromatic ring, solvent polarity, and a proper match between the π surfaces of the complementary D and A units. Experimental techniques based on UV/vis and NMR spectroscopy have been most commonly used to determine the association constants of D–A complexes. In a few cases isothermal titration calorimetry (ITC) has also been employed for direct estimation of the thermodynamic parameters associated with CT complexation. A detailed discussion related to different methods for determination of association constants and a comprehensive account of thermodynamic parameters for various D–A complexes have been reviewed elsewhere.[27,56] However, as a separate CT absorption band, solely resulting from the associated species, appears in the UV/vis spectra, monitoring its intensity as a function of concentration appears to be a convenient method for estimating the association constant of a 1:1 D–A complex using Equation 1,[57] where c and A represent the concentration of individual components in a 1:1 D/A mixture and absorbance (CT band), respectively, and l is the optical path length. The values of c and A are determined experimentally by a series of UV/vis experiments with different dilutions. Then from the slope and intercept of the linear plot of c/A against $1/A^{1/2}$, one can estimate the association constant (K) and molar extinction coefficient (ε) of the CT complex.

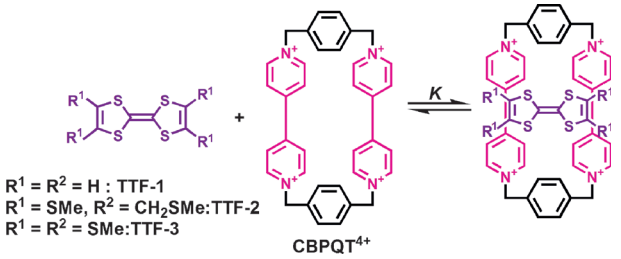
$$\frac{c}{A} = \left(\frac{1}{K\varepsilon l}\right)^{1/2} \frac{1}{A^{1/2}} + \frac{1}{\varepsilon l} \qquad (1)$$

Table 1: Association constants (K) for a selection of D–A pairs listed in Scheme 2.

D–A pair	Solvent	T [°C]	K [M^{-1}]
D1–A1	cyclohexane	20	13.5 ± 0.4
D1–A1	CCl_4	20	5.7 ± 0.3
D1–A1	chloroform	20	0.76 ± 0.05
D1–A4	CCl_4	33.5	15.4
D2–A4	CCl_4	33.5	4.90
D5–A8[a]	$CDCl_3$	25	12.0
D5–A9[a]	$CDCl_3$	25	42.0
D11–A11[a]	CH_2Cl_2	[b]	$2.6(\pm 0.8) \times 10^4$

[a] Derivatives with different R groups have been used for the complexation studies. [b] Not mentioned.

Herein we show a few examples (Table 1) to highlight some important aspects related to structural and solvent effects on association constants. Based on the extensive experimental data it is grossly accepted that higher K values can be obtained in poorly ionizing solvents. For example the K value of the D1–A1 complex[58] (Table 1) in cyclohexane is about 20 times higher than that in $CHCl_3$. However apart from polarity alone, other structural parameters of the solvent molecules may also influence the position of the equilibrium. For example solvents like THF and ethers can act as n donors and other solvents (even chloroform) may be involved in weak hydrogen bonding with the D/A chromophores and thus the estimated K values for a particular D–A pair may not always show a linear relationship with the solvent dielectric constant.[27] For example, K for the D1–A4[27] is 15.4 M^{-1} (Table 1), which is about three times higher compared to that of D1–A1 in the same solvent (CCl_4). This can be attributed to the more electron-deficient nature of A4 compared to A1. Likewise with a fixed acceptor, A4, D2 exhibits a lower K value[27] compared to D1 because of a fewer number of electron-donating methyl groups in D2. Stoddart and co-workers systematically studied[59] CT complexes of a series of TTF derivatives (Scheme 3) with cyclobis



Scheme 3. Chemical structure of TTF derivatives, $CBPQT^{4+}$, and their CT complex.

(paraquat-*p*-phenylene) ($CBPQT^{4+}$) as an acceptor, to understand the influence of the donating ability of the TTF units and other structural parameters on K.

Part of their investigations showed the remarkable effect of the first redox potential ($E^1_{1/2}$) of the TTF donors on the observed K values (Table 2). For example, in MeCN going from TTF-3 to TTF-1 with a decreasing $E^1_{1/2}$ value, the

Table 2: Association constants (K) for various TTF derivatives (see Scheme 3) with $CBPQT^{4+}$ estimated by NMR experiments ($T = 30$ °C).

TTF	Solvent	K [M^{-1}]	$E^1_{1/2}$ [V] (MeCN)
TTF-1	MeCN	10000	+0.34
TTF-2	Me_2CO[a]	490	+0.45
TTF-3	MeCN	180	+0.51

[a] Data not reported in MeCN.

K value increases by almost two orders of magnitude. Although it is not appropriate to compare the absolute magnitude of K values of these interlocked systems with those reported in Table 1, the observed trend certainly can be considered a good example of a significant effect of the donating ability of D on the binding constants for a particular set of D–A complexes. Beside electronic effects, the proper matching between the complementary π surfaces also significantly influences the association properties. For example, D5 shows a higher binding affinity towards A9 compared to that with A8[60] (Table 1) although both the acceptors contain two imide groups. This can be attributed to a more effective π overlap in the D5–A9 CT complex. Chai, Liu, and co-workers reported[52] a remarkably high association constant (Table 1) for D11–A11 resulting from complementary charge distribution and perfect shape matching in this D–A pair. This value is one of the highest association constants reported to date for any D–A complex which lacks additional assistance from other noncovalent interactions. Wilson and co-workers have recently reported[61] a systematic study on co-assembly between a series of homopolymers containing different pendant donors (carbazole, phenothiazine and pyrene) and acceptors (pyromellitic diimide, naphthalene diimide, and perylene diimide), and based on the experimental findings they identified pyrene–NDI (D7–A9) as the best D–A pair among all tested D–A combinations within this series. Noteworthy in this case, is that the difference of π-surface area is within only 10 % for the other two donors. Thus the difference in K values was attributed to the highly congruent HOMO of pyrene and LUMO of NDI, thus resulting in an effective HOMO–LUMO overlap in alternate cofacial stacking. While the majority of the studies concerning association constants of CT complexes have been conducted in organic solvents, Iverson and co-workers have shown[62] a strong and positive impact of high polarity solvents such as MeOH and H_2O on alternate D–A stacking of the D5–A9 pair by ^1H NMR experiments. The K values increased by almost three orders of magnitude (Table 3) by changing the medium from $CDCl_3$ to D_2O.

They examined the thermodynamic parameters for the CT-complex formation in a range of other solvents having intermediate polarities and correlated the estimated K and ΔG^o values with the empirical solvent polarity parameter $E_T(30)$, thus demonstrating higher stability in polar solvents, a trend which is an exactly opposite to that seen in the data reported in Table 1. This opposite behavior indicates that in low polarity solvents the association constants show an inverse relationship with the dielectric constant of the solvent because of dominant electrostatic forces, while in highly polar solvents such as MeOH and H_2O, strong solvophobic

Table 3: Solvent effect on D5–A9 binding parameters at $T = 298$ K.

Solvent	$E_T(30)$ [kcal mol^{-1}]	K [M^{-1}]	$-\Delta G°$ [kcal mol^{-1}]
$CDCl_3$	39.1	$2 \pm < 0.5$	0.4
[D_6]acetone	42.2	$8 \pm < 0.5$	1.2
[D_6]DMSO	45	$3 \pm < 0.5$	0.7
CD_3CN	45.6	$11 \pm < 0.5$	1.4
CD_3OD	55.5	$30 \pm < 0.5$	2.0
CD_3OD/D_2O (3:1)	57	63 ± 2	2.5
CD_3OD/D_2O (1:1)	58.9	254 ± 41	3.3
CD_3OD/D_2O (1:3)	60.8	952 ± 64	4.1
D_2O	63	2045 ± 63	4.5

[a] Empirical solvent polarity parameter for nondeuterated solvents.

repulsion leads to very stable alternate D–A π stacking which corroborates well with literature reports on self-assembly of other π systems.[63,64]

3. Gelation Driven by CT Interactions

Low-molecular-weight supramolecular gelators have been a topic of recent interest[65–68] owing to their fascinating self-organization properties and relevance in a range of applications including drug delivery, light harvesting, templating, organic photovoltaics, and others. D–A CT-interaction-promoted gelation has been studied in the recent past by many groups[69–78] including ours.[79,80] Gelation promoted by CT interactions was first reported by the group of Maitra in 1999.[69] They examined co-assembly of a few donor units, having appended bile acids (Figure 1), in the presence of the electron-deficient chromophore trinitrofluorenone (TNF, **1f**) and they noticed CT-interaction-promoted gelation for TNF with compounds **1a**–**c**. In suitable solvents, the critical gelation concentration (CGC) was found to be even less than 1 wt%, thus suggesting supergelation. However the gel-to-sol transition temperature (T_g) of **1a**/**1f** (1:1) was estimated to be only 35 °C in $CHCl_3$ ($c = 62$ mM of each component), thus suggesting poor thermal stability. Moreover **1d** and **1e** do not produce a gel, thereby suggesting that the placement of the donor unit on the bile acid backbone played a critical role for

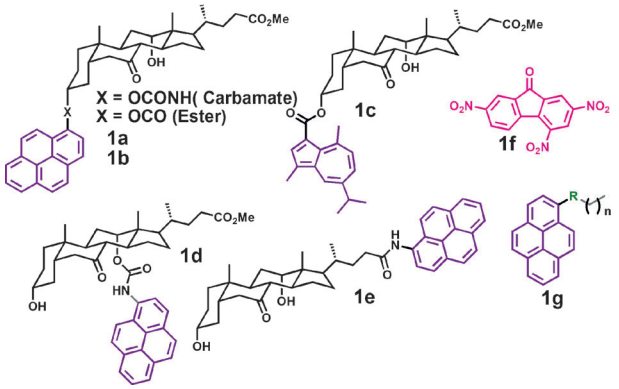


Figure 1. Early reports on various D and A building blocks for gelation promoted by CT complexation.[69–72]

co-assembly and gelation. Subsequently, they studied the co-assembly of pyrene derivatives, with appended alkyl chains (**1g** where R is different functional groups), and TNF in the absence of the bile acid backbone.[70] Interestingly, pyrene derivatives lacking any hydrogen-bonding groups show CT gelation but those with the amide, urethane, or urea groups prefer self-assembly rather than co-assembly with TNF. Subsequently more reports have appeared on the gelation of different D–A pairs and describe the relationship between gelation properties and the molecular structure of the building blocks, nature of the solvent, and the D/A stoichiometry.[71–74]

While these examples deal with gelation by only CT interactions, there is a significant interest in additionally using other supramolecular forces, such as hydrogen bonding, for formation of fibrillar two-component assemblies. TTF and its derivatives[75–77] are well-known donors with electroactive properties. They can be electrochemically/chemically oxidized to radical cations and dications, thus providing an additional opportunity to tune their self-assembly by an external stimuli. Zhu and co-workers[75] reported spontaneous gelation of a urea-functionalized TTF (**2a**, Figure 2A) in 2-propanol, cyclohexane, and 1,2-dichloroethene (DCE).

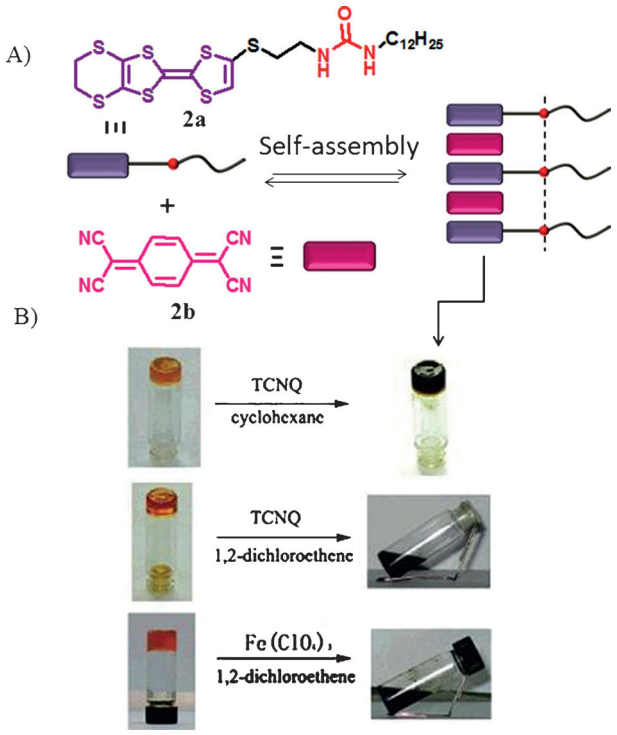


Figure 2. A) TTF gelator and mode of co-assembly with TCNQ. B) Solvent-dependent effect of TCNQ on TTF gelation (top and middle) and oxidation-induced gel-to-sol transition (bottom). Reprinted with permission from (Ref. [75]). Copyright (2005) American Chemical Society.

Solvent polarity seems to play a key role on how the TTF–TCNQ CT complex influences the gelation behavior. In a highly apolar solvent cyclohexane, the TTF gel shows morphology transition from fibers to tubes in the presence of TCNQ (**2b**) with concomitant appearance of a deep green

color (Figure 2B) owing to CT complexation. Surprisingly, in another solvent such as DCE, addition of TCNQ destroys the gel phase of TTF and produces a dark green suspension (Figure 2B). Such contrasting behavior in two different solvents can be attributed to the presence of more charge on the TTF gelator in a more polarizable solvent such as DCE. Chemical oxidation of the TTF chromophore by an equivalent amount of $[Fe(ClO_4)_3]$ also destroyed the gel phase (Figure 2B) because of electrostatic repulsion among the positive charges of the oxidized TTF product.

Smith and co-workers reported metastable gelation of styrene/divinylbenzene (90:10) by a dimeric amide-functionalized pyrene donor (**3a**, Figure 3) only in the presence of

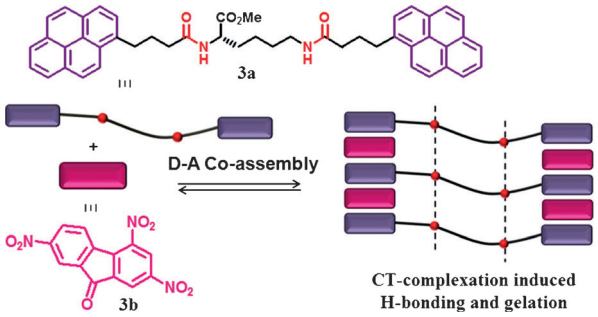


Figure 3. Gelation promoted by simultaneous hydrogen bonding and CT interactions.

a TNF acceptor (**3b**).[78] In this case a low T_g value (34 °C at $c = 20$ mM of **3a**; **3a**/**3b** = 1:2) indicates a weak assembly. Spatial organization of the building blocks in alternating D and A units appears to be essential for the amide groups to remain hydrogen bonded, and this was not the case for homoaggregates of the pyrene dimers. Interestingly, the fibrillar gel network gradually transforms into microcrystals through fiber–fiber aggregation, thus indicating an intimate relationship between gelation and crystallization.[67]

We have explored co-assembly of a bis(trialkoxybenzamide)-functionalized dialkoxynaphthalene (DAN) donor and naphthalene diimide (NDI) acceptor gelators (Figure 4A) with different spacer lengths (L_1 and L_2 for A and D chromophores, respectively) between the two amide groups.

All compounds (shown in Figure 4A) on their own exhibit spontaneous gelation[79,80] in a nonpolar solvent such as methylcyclohexane (MCH). The choice of such building blocks stems from the fact that it can impart self-assembly in a nonpolar solvent through the synergistic effects of hydrogen bonding among the amides, π–π stacking/CT interactions between the D and A chromophores, and hydrophobic effects through the terminal trialkoxybenzamide groups. We observed that the mode of assembly in such systems strongly depends on the subtle balance between several factors. For the D–A pair, where the relative distance between the two amides in the D and A chromophores does not match ($L_1 \neq L_2$), self-sorting[81] is observed[82] and is stabilized by π–π stacking and strong hydrogen bonding between similar A–A and D–D chromophores. When the distances are comparable

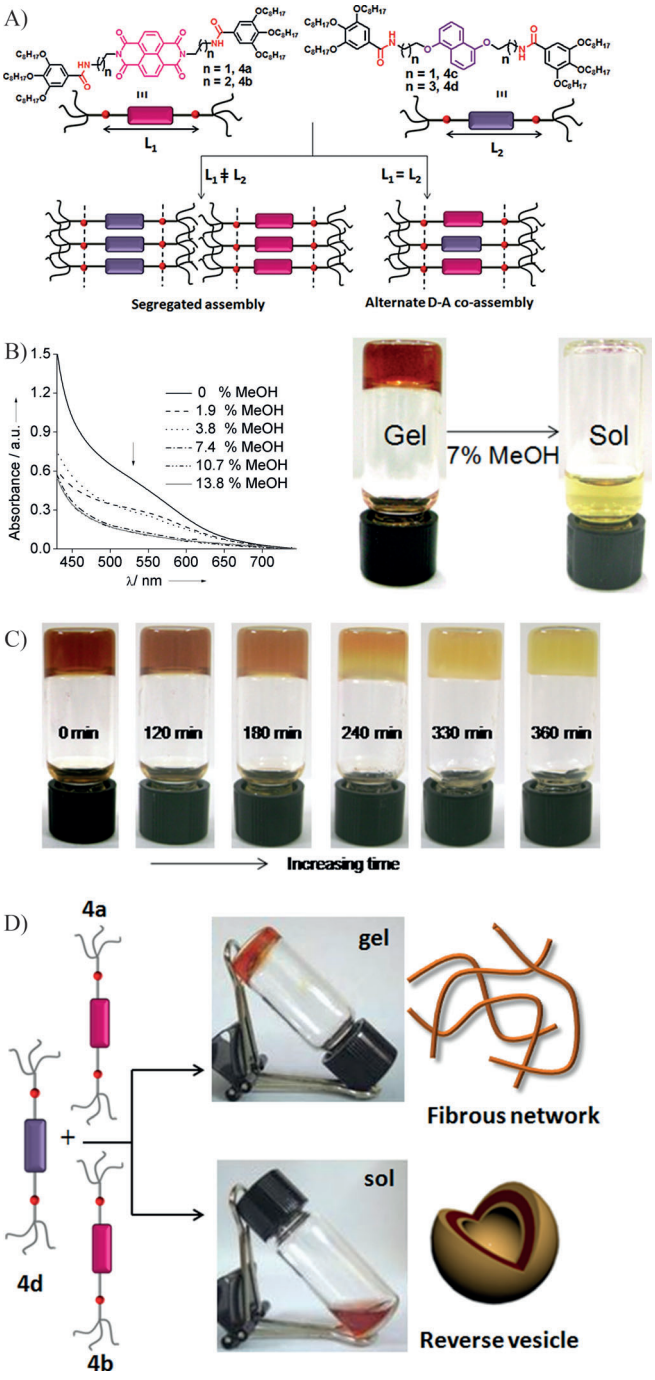


Figure 4. A) Structure of NDI- and DAN-based building blocks and mode of assembly. B) Effect of MeOH on the CT absorption band (left) and gelation (right) of **4a**/**4d** in TCE. C) Supramolecular switching of CT gel (**4a**/**4d**) to self-sorted gel in MCH. D) Structure-dependent morphology and gelation of D–A CT complexes. Figures 4B and C are reprinted with permission from (ref [80]). Copyright (2011) John Wiley and Sons.

($L_1 \approx L_2$), both possibilities exist:[79,80] a) Alternate D–A stacking which is stabilized by moderate hydrogen bonding (because the distance is nearly but not exactly same), between the amides of dissimilar D and A chromophores, and CT interactions, b) self-sorting that involves the hydrogen bonding without any geometrical constraints and π stacking between similar chromophores.

In a moderately polarizable solvent like tetrachloroethylene (TCE), where the hydrogen bonding is inherently less influential, the contributions of both CT interactions and hydrogen bonding count and thus a stable red CT gel is formed[79] (Figure 4B) from **4a**/**4d** (1:1) with a critical gelation concentration of (CGC) = 3.0 mM and T_g = 72 °C (c = 10 mM of each component). Significantly high thermal stability of the CT gel in this case, compared to previous reports,[69,78] is believed to be a consequence of intermolecular hydrogen bonding between the amide groups in the alternately stacked D–A assembly. This presumption is supported by the observation that the CT gel in TCE is destroyed (Figure 4B) with concomitant disappearance of the CT band in the presence of only about 7% (v/v) MeOH, which is a protic solvent that competes for hydrogen bonding. Unlike TCE, in a less polarizable solvent such as MCH, where hydrogen bonding is expected to be stronger, the mode of assembly is governed solely by hydrogen bonding and the relatively weaker CT/π-stacking interactions do not play a decisive role. Therefore, in MCH although initially a kinetically controlled red CT gel is formed by a **4a**/**4d** pair, within 5–6 hours it reorganized to the thermodynamically more-stable self-sorted yellow gel (Figure 4C) to achieve maximum effect of the hydrogen bonding. This reorganization was supported by FT-IR studies which showed a shift of the peak corresponding to the NH stretching from 3309 cm^{-1} to 3271 cm^{-1} as a result of such supramolecular chromophoric reorganization. Stability and morphology of the CT complexes and the rate of supramolecular switching (from CT to segregated state) are greatly influenced by even minor structural variations of the building blocks, solvent polarity, and the DAN/NDI ratio.[80] For example, in a given D–A pair, the introduction of just one additional methylene unit to the spacer segment of the NDI building block leads to a complete change in the morphology, and gelation behavior which can be observed in Figure 4D. In TCE, the DAN building block **4d** forms one-dimensional (1D) fibers and 2D reverse vesicles (sol) with **4a** and **4b**, respectively, and consequently gelation is noticed selectively for the **4d**/**4a** pair. Association constants for co-assembly of **4d**/**4b** (sol) and **4d**/**4a** (gel) were estimated[80] to be 1300 M^{-1} and 342 M^{-1}, respectively, in TCE at T = 25 °C. Notably an association constant value on the order of about 10^3 M^{-1}, as obtained for **4d**/**4b**, is the highest reported so far for any NDI–DAN pair in organic solvents and can be attributed to the additional stability of the D–A stack imparted by hydrogen bonding. However Figure 4D reflects stronger assembly is not the sole criteria for gelation even for structurally very similar building blocks. Rather in this case the anomaly between the stability of the D–A complex and gelation can be attributed to a slight difference in the flexibility of the spacer segments, with even one additional methylene unit, by which **4a** and **4b** can be structurally differentiated.

4. Amphiphilic CT Complexes

Amphiphilic small molecules[83] and macromolecules[84] produce versatile nanostructured assemblies in aqueous medium. The nature of the aggregates and their functional utilities are closely related to the structure of the amphiphile. Structural engineering of amphiphilic molecules has been mostly limited to variation in the volume or area of the hydrophobic tail or hydrophilic head groups. Inclusion of a specific supramolecular functional group in an amphiphilic molecule may help in achieving more diversity in their aggregation properties[85] by virtue of directional noncovalent interactions.

Zhang and co-workers showed[86–89,92,93] CT interactions could substantially modulate aggregation properties of D/A-containing amphiphiles. For example, a pyrene-functionalized cationic surfactant (**5a**, Figure 5A)[87] exhibits nanotubular assembly by π stacking of the pyrene chromophores. But, in the presence of an acceptor (**5b**, Figure 5A), a transparent

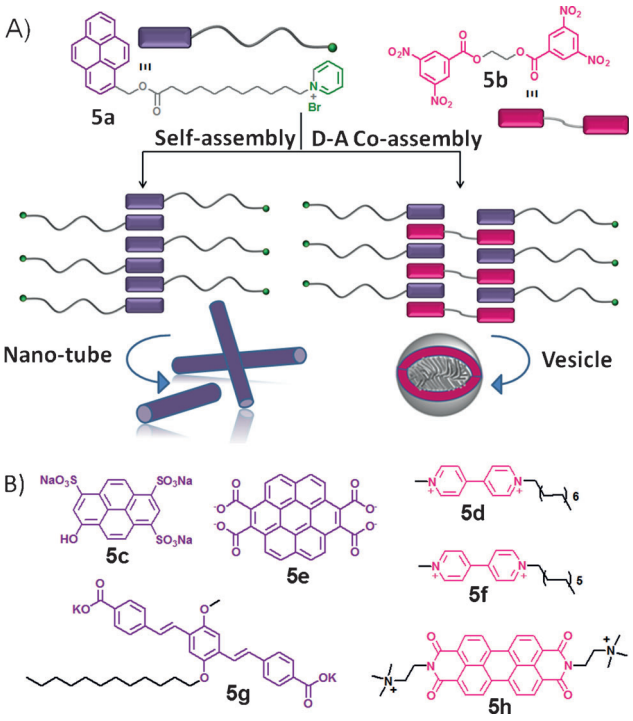


Figure 5. A) Nanotubular assembly of pyrene-functionalized surfactant and its morphology transition to spherical vesicles by CT interactions in presence of an acceptor. B) Structure of various other donor and acceptor amphiphiles studied by the groups of Zhang (**5c**, **5d**) and George (**5e**, **5f**, **5g**, and **5h**).

yellow solution is observed owing to the CT complexation which induces morphology transformation from nanotubes to vesicles because of the relatively shorter radius of curvature for the alternately stacked D–A assemblies.

In a subsequent report they described co-assembly of a viologen-containing amphiphile (**5d**, Figure 5B) with a water-soluble anionic pyrene donor (**5c**, Figure 5B). Unlike the previous example (Figure 5A), in this case **5d** forms spherical vesicles[88] while its CT complex with **5c** exhibits elongated fibers with a pH-dependent curly or straight morphology. In a more recent report they further elaborated on pH-dependent aggregation of amphiphilic CT complexes generated from similar chromophores.[89]

By using similar strategies George and co-workers have reported formation of a hydrogel by co-assembly of a coronene tetracarboxylate salt donor (**5e**, Figure 5B) and dodecyl methyl viologen acceptor (**5f**, Figure 5B).[90] They have also shown[91] co-assembly of a *p*-type semiconducting oligo(phenylenevinylene) (**5g**, Figure 5B) donor and an *n*-type semiconducting perylenebisimide (**5h**, Figure 5B) acceptor which produces cylindrical micelles leading to hydrogelation at higher concentrations. Conductive atomic force microscopic studies on a selected gel fiber reveal remarkably high conductivity ($0.02\,S\,cm^{-1}$), thus suggesting great prospects for these materials in organic electronic devices.

In a different design, Zhang and co-workers have shown strong influences of a minor structural variation on the co-assembly of donor- and acceptor-containing surfactants (Figure 6). Individually, **6a** and **6b**[92] show fibrillar and spherical

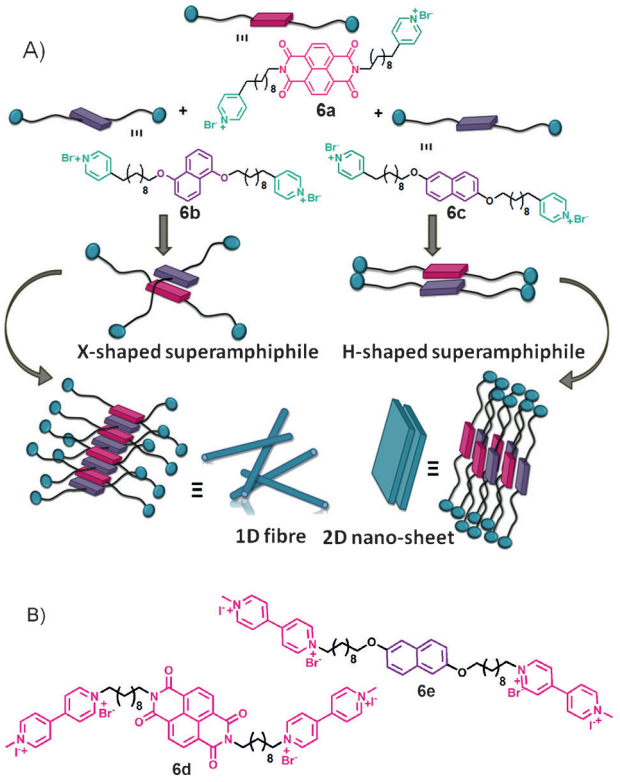


Figure 6. A) Geometry-dependent aggregation of NDI–DAN superamphiphiles. B) Structure of terminal acceptor containing donor and acceptor surfactants reported in Ref. [93].

micellar morphologies, respectively, in aqueous medium. In contrast, their equimolar mixture exhibits a rodlike morphology owing to formation of an X-shaped superamphiphile[85] through alternate D–A stacking driven by CT interactions. In contrast, **6c** (Figure 6), which differs from **6b** by only the position of the two alkoxy substitutions, forms a H-shaped D–A complex with **6a** because of the directional nature of the CT interactions, thus resulting in a 2D nanosheet morphology. They further extended the scope of this superamphiphile design by linking two viologen acceptor units (Figure 6B) at the termini of the **6a** and **6c** building blocks.[93]

The combination of **6d** and **6e** also shows a 2D sheetlike morphology similar to that of **6a**/**6c**. But because of the presence of the terminal acceptor units, the structure can be transformed into a 1D fiber in the presence of a pyrene donor owing to additional CT interactions involving the pyrene and the terminal viologen units. These examples illustrate ample opportunity to tune the aggregation properties of amphiphilic molecules through CT interactions.

In this section so far we have discussed mixed assemblies of alternately stacked D and A amphiphiles by solvophobically assisted CT interactions. We envisaged that involving hydrogen-bonding functional groups could further enhance the possibility of tuning the aggregation phenomenon in such π-conjugated amphiphiles. With this aim we have studied the self-assembly of an electron-deficient naphthalene-diimide-based amphiphile (NDI-1, Figure 7),[94] which contains two hydrophilic trialkoxy benzhydrazide wedges on both arms of the chromophore for enhancing water solubility, and two hydrazide groups for hydrogen bonding. In aqueous medium, it spontaneously forms vesicles (Figure 7) through the syner-

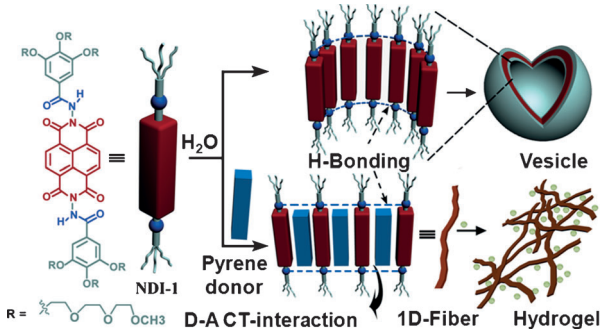


Figure 7. Self-assembly of hydrazide-functionalized NDI bolaamphiphile and morphology transition through pyrene intercalation by CT interactions. Reprinted with permission from (Ref. [94]). Copyright (2012) John Wiley and Sons.

gistic effect of π stacking and hydrogen bonding. Control experiments show the necessity of the rigid placement of the hydrazide groups in the hydrophobic pocket to ensure hydrogen bonding between themselves instead of bulk water. Further, we have shown that the electron-deficient NDI-1 can allow intercalation of a water-insoluble electron-rich pyrene donor by virtue of strong CT interactions ($K = 9.69 \times 10^3\,M^{-1}$). Importantly, even in the alternately stacked CT state the hydrogen-bonding network among the hydrazides remains unaffected. But in this arrangement, increase in radius of curvature,[95] as a result of pyrene intercalation, induces a gradual morphology transition from vesicles to 1D fibers, thus resulting in increased viscosity and eventually gelation after 72 hours.

In an attempt to utilize this intercalation phenomenon for surface functionalization of the NDI vesicle, we tested intercalation of a carboxylate-functionalized water-soluble pyrene derivative which also showed similar effects with a linear relationship between the amount of added donor and the intensity of the CT absorption band. Zeta-potential measurements revealed varying surface charges as a result

of a different amount of added pyrene containing a carboxylate functional group. This result provides an opportunity for further surface modification of similar NDI vesicles through D–A CT interactions by intercalation of various functionalized pyrenes.

5. Foldamers and Conformationally Restricted Macromolecules

Synthetic oligomers/macromolecules that adopt well-defined conformations in solution are known as foldamers.[41,96–99] For achieving an organized folded assembly, the entropy cost needs to be compensated for by the enthalpy gain with contributions from intrachain noncovalent interactions such as hydrogen bonding. While nature has executed it with perfection, it still remains a challenging task to obtain a well-defined secondary structure of synthetic polymers/oligomers, particularly those with a flexible backbone because of their numerous conformations in solution. Intrachain CT interactions between D and A units embedded in a single chain has been utilized to recognize such folded assemblies. Iverson and co-workers demonstrated the folding of a series of D–A oligomers with varying chain length where the DAN and NDI chromophores were linked by flexible amino acid linkers containing a pendant carboxylic acid functional group.[100] UV/vis studies showed a reduction in band intensities and the appearance of a red-shifted CT band with higher oligomers, thus suggesting the existence of the folded structure by intrachain D–A stacking (Figure 8), which was

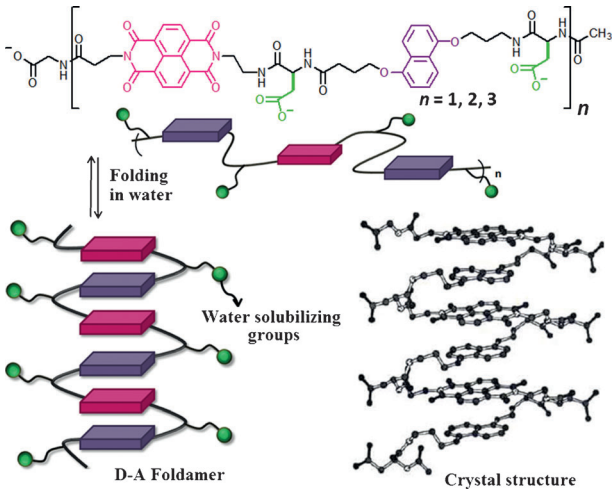


Figure 8. Folding of D–A oligomers (top) in aqueous medium by intrachain CT interactions. Crystal structure is shown at bottom right. Reprinted by permission from Macmillan Publishers Ltd: [NATURE] (Ref. [100]), copyright (1995).

also confirmed by a change in the chemical shift values of the aromatic ring protons and NOE studies. In a subsequent report, they showed that such folded structures can undergo an irreversible thermal denaturation,[101,102] a phenomenon which is similar to the denaturation of proteins. The same group has studied various other structurally related D–A oligomers with different molecular designs for gaining detailed insight into the folding process.[54,103]

In an interesting finding, Iverson and co-workers compared the folding patterns of a few D–A oligomers (Figure 9) having different D–A sequences. Oligomers having a DAD sequence forms a pleated structure, while a DDA-type system shows an intercalative folding pattern.[104]

They also demonstrated that such folding can be achieved by interchain CT interactions between (Figure 10) structur-

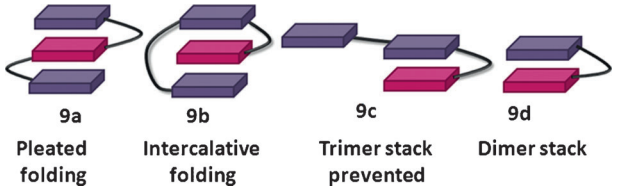


Figure 9. Sequence-dependent folding of different D–A oligomers.

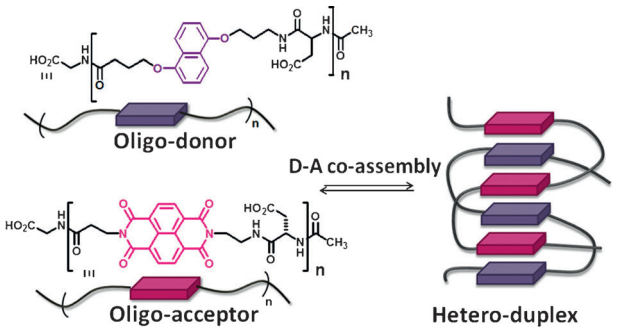


Figure 10. Heteroduplex formation by folded donor and acceptor oligomers.

ally similar oligomers containing either NDI or DAN units.[105] They studied the effect of the length of the oligomers on the thermodynamic parameters for the formation of the double-helical structure by NMR spectroscopy and isothermal titration calorimetric (ITC) experiments, which revealed a 1:1 stoichiometry between the NDI and DAN oligomers. Stability constants at 318 K were found to be $3.5\ (0.2)\times 10^5\,\text{M}^{-1}$ and $1.3\ (0.1)\times 10^2\,\text{M}^{-1}$ for the longest ($n=4$) and shortest ($n=1$) oligomers, respectively. Such remarkable effects of chain length on binding affinities can be attributed to the multivalent effect which becomes increasingly prominent for higher oligomers.

Li, Chen, and co-workers studied the folding of oligopeptides containing pendant DAN donors and pyromellitic diimide acceptor units, and showed a stable folded conformation in solution by virtue of D–A interactions.[106]

Ramakrishnan and co-workers showed that CT interactions in concurrence with other noncovalent forces can promote folding of even high-molecular-weight polymers[107–114] with a flexible backbone. They considered self-assembly of a segmented donor–acceptor polyimide (Figure 11 A), consisting of an alternately placed pyromellitic diimide (PMD) acceptor and a DAN donor, connected by a hydrophilic hexa(ethylene oxide) (OE) spacer.[107] In the presence of a suitable alkali-metal ion such as K^+, which can

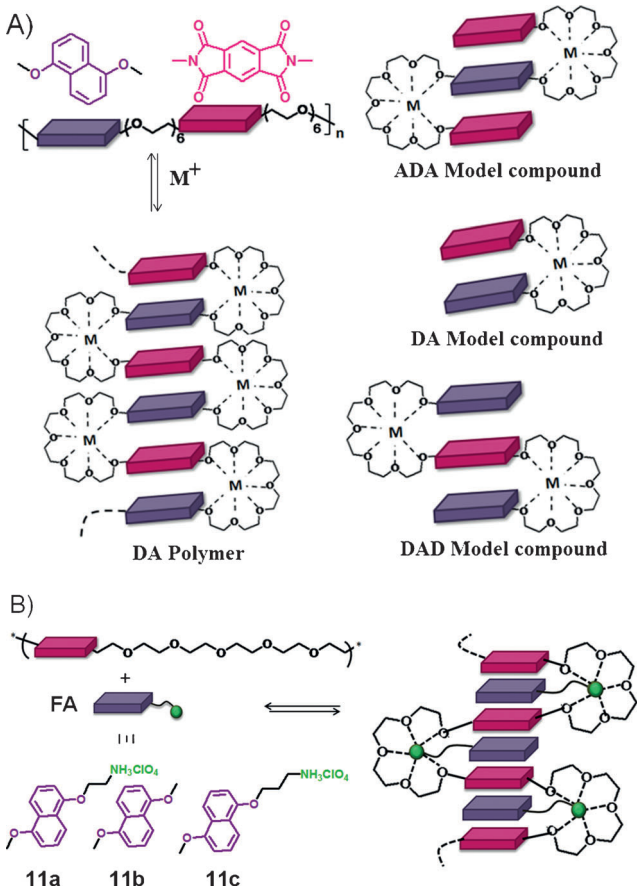


Figure 11. A) Metal ion complexation induced CT interaction and folding of D–A polymers and model compounds. B) External FA induced folding of a flexible polymer.

effectively form a complex with the OE spacer, the polymer adopts a folded conformation in relatively polar organic medium (1:1 $CHCl_3/CH_3CN$) owing to synergistic effects of the CT interactions, metal-ion complexation, and solvophobic assistance. In a solvent-dependent ($CHCl_3$/MeOH mixtures) folding study they noted non-unidirectional behavior which is discussed in Section 2. Subsequently they have studied the folding of structurally similar polymers with varying spacer segments and found alkali metal ion selective folding for the different OE-spacer-containing polymers.[108] A comprehensive spectroscopic investigation with DAD-, ADA-, and DA-type model compounds indicates that in the folded conformation, the D and A units of the polymer experience similar chemical environments to that of the ADA and DAD model compounds, respectively. This suggests appreciable average stack lengths for the folded polymer.

Subsequently they introduced an external folding agent (FA) which could induce folding of a polymer containing only acceptor units (Figure 11 B) by a two-point binding, including the CT interaction and complexation of the ammonium ion of the FA (**11a**) with the OE spacer of the polymer chain.[109] Association constants (from NMR experiments in 1:1 $CDCl_3/CH_3CN$) for the two structurally related FAs, **11a** and **11c**, were estimated to be 850 M^{-1} and 600 M^{-1}, respectively, thus suggesting that proper choice of the spacer segment is important for effective binding. More interestingly a physical mixture of **11b** and NH_4ClO_4 shows an association constant of only 30 M^{-1} with the acceptor polymer, thus reflecting the importance of synergy between the two different noncovalent forces.

Such an FA-based approach was also successfully employed later in a slightly modified design involving CT interactions and hydrogen bonding (Figure 12).[110] In this case

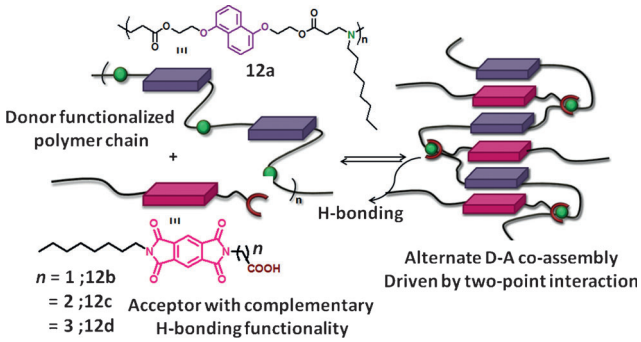


Figure 12. Externally induced folding of a synthetic polymer by two-point interactions involving hydrogen bonding and CT interactions.

a donor-containing polymer (**12a**) could be made to adopt a folded conformation in the presence of **12c**, which contains an acceptor unit and a complementary hydrogen-bonding group. An appreciably high association constant (1200 M^{-1}) is reported for **12a**/**12c** in $CHCl_3$/MeOH (20:1) because of the synergistic effect of the CTinteractions and hydrogen bonding. Interestingly, the *K* values for complexation of **12a** with **12b** and **12d** are much less (800 M^{-1} and 300 M^{-1}, respectively), thereby reflecting the vital role of the number of methylene units in the acceptor chromophore for effective two-point interactions.

Hybridization of these two designs (metal-ion-induced folding of a D–A polymer and FA-driven folding of only an A polymer) in a single system[111] allows stepwise folding of the polymer chain containing randomly distributed D–A and A–A segments (Figure 13). In the presence of a suitable alkali-metal ion the polymer exhibits a partially folded conforma-

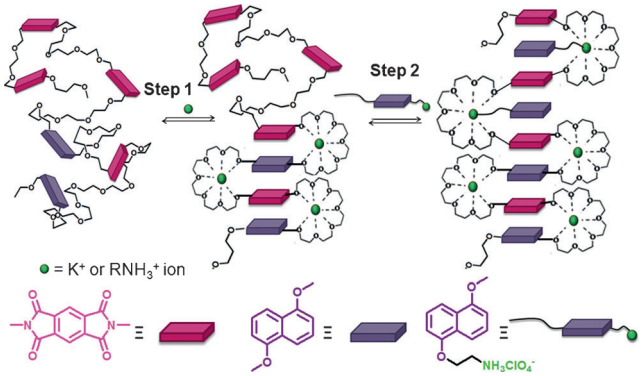


Figure 13. Two-step folding of a synthetic polymer having D–A and A–A sequences.

tion (Step 1) by intrachain CT interactions between the adjacent D–A units. Subsequent addition of the FA induces folding (Step 2) of the remaining segments containing A–A sequences.

This concept of CT-interaction-promoted folding in synthetic polymers was also explored in aqueous medium with ionenes containing alternate D and A units.[112] Strong solvophobic repulsion induces a chain collapse in rather controlled manner by alternate D–A stacking. In a very recent report George and co-workers have combined amphiphilicity and an FA-based strategy together to demonstrate possibility of multiple-acceptor binding to a single-donor scaffold in aqueous medium.[115]

The story of polymers containing pendant D/A units is rather old. However in the early days the focus was on their enhanced charge-transport properties as a result of D–A stacking.[116–118] The concept of supramolecular assembly in such macromolecular systems was probably demonstrated first by Percec and co-workers.[119] They studied solid-state miscibility of polymers (Figure 14) bearing a carbazole donor

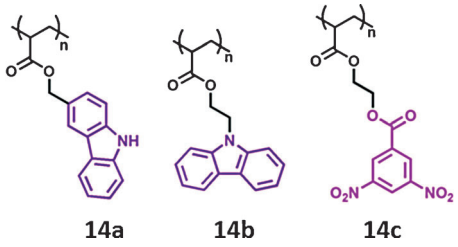


Figure 14. Early examples of polymers containing pendant aromatic donor or acceptor units.

(**14a**, **14b**) and dinitrobenzoate acceptor (**14c**) by using detailed thermal analysis. The glass-transition temperature of a blend of the two polymers showed a positive deviation compared to the weight-average value estimated from those of the individual components. This was attributed to the effective D–A CT interaction.

Rotello and co-workers showed that it is possible to impose a restriction on the conformational freedom of a flexible polymer backbone in solution through intermolecular CT interactions (Figure 15).[120] They showed a polystyrene derivative (**15**) containing pendant anthracene units can adopt a globular conformation by weak intrachain π-stacking interactions between the anthracene chromophores attached to the same chain. Furthermore, in the presence of picric acid, an electron acceptor, the stability of the collapsed polymer globule can be enhanced significantly through CT interactions between the picric acid and anthracene. Unlike this example, which shows assembly of a single polymer chain, Kilbinger and Grubbs showed physical crosslinking of several polymer chains, containing a pyrene donor at the chain terminus, in the presence of perfluoroarene acceptors through CT interactions,[121] thus resulting in network formation and hydrogelation.

More recent reports portray supramolecular assemblies of two different polymers containing multiple pendant chromophores of either an electron-rich or electron-deficient nature. Iverson and co-workers have shown[122] that multivalent interchain D–A interactions between water soluble polymers containing NDI and DAN pendants can produce a network structure (Figure 16) through CT interactions, thus resulting

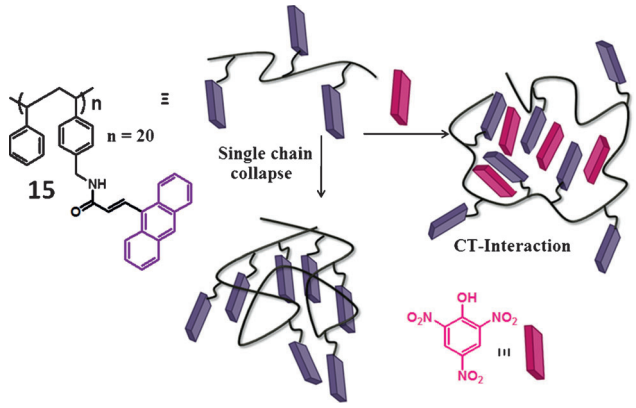


Figure 15. Intrachain collapse of macromolecules by π stacking and stabilization of the collapsed structure through CT interactions.

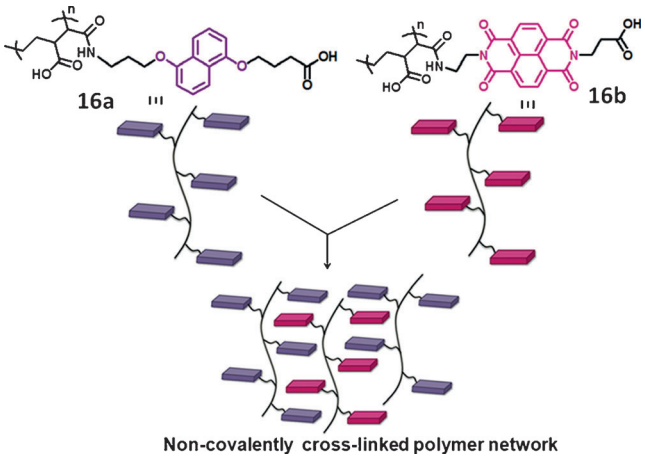


Figure 16. CT-promoted network formation of polymers with appended donors and acceptors.

in a purple viscous liquid. Conceptually similar strategies with different polymer scaffolds have been also reported by Weck and co-workers[123] as well as Wilson and co-workers[124] for organic solvents.

From a broader perspective, systems described so far in this section show either intrachain folding or interchain crosslinking through CT interactions. Colquhoun and co-workers studied a slightly different system which encompasses both of these features. They showed a high binding affinity of a molecular tweezer containing two bisamide-functionalized pyrene donors and a pyromellitimide acceptor by simultaneous hydrogen bonding and CT interactions (Figure 17).[125] Their studies reveal enhanced binding strength of the tweezer molecule with pyromellitimide, attached to compounds containing a 4,4′-biphenylenedisulfone unit, because of the additional π-stacking interactions with the latter chromophore.

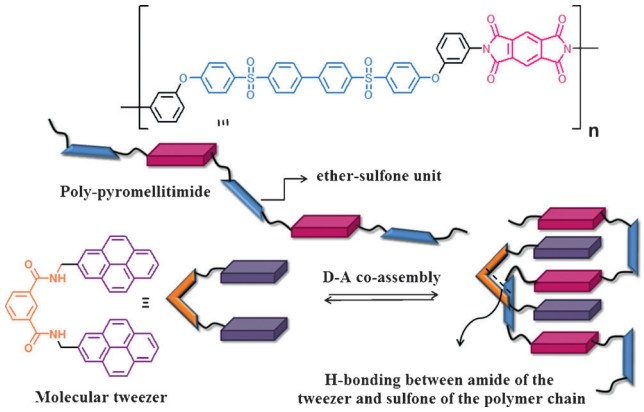


Figure 17. Assembly of donor tweezer and acceptor polymer thorugh CT interactions.

This strategy was extended later to the macromolecular systems wherein specific complementary D–A binding motifs could help in determining the sequence of high-molecular-weight polymers[126] in the short as well as long range.[127,128] This group further utilized the pyrene–NDI alternate stacking interaction to demonstrate supramolecular crosslinking of a folded polymer. The system consists of a polyamide backbone with pyrene groups at both ends while the folding of the other polymer is achieved by intrachain π-stacking interactions between the NDI units.[129] A blend of these two polymers shows superior mechanical properties resulting from the supramolecular crosslinking by the D–A CT interactions (Figure 18) and also self-healing properties by taking advantage of the noncovalent nature of crosslinking.

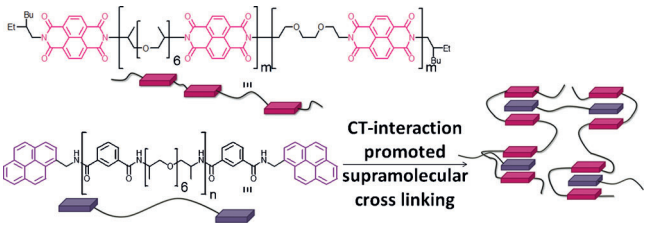


Figure 18. Supramolecular crosslinking by D–A interactions.

Colquhoun and co-workers also examined the mechanical properties of blends made out of the same NDI folded polymer and similar telechelic polyamides having end functionalization using a pyrene-containing tweezer.[130] In this case mechanical properties of the blends are found to be much higher compared to the previous systems because of the stronger binding between the NDI and pyrene tweezer.

In a very recent report,[131] Sada and co-workers have shown tunable lower critical solution temperature (LCST) properties of a polymer containing pendant donor units (pyrene) in organic solvents through CT interactions (Figure 19). In a solvent like 1,2-dichloroethane the polymer **19a** is not soluble on its own because of the presence of the rigid aromatic units. However, in presence of an acceptor (**19b–d**), derivatized with branched alkyl chains, the resulting CT

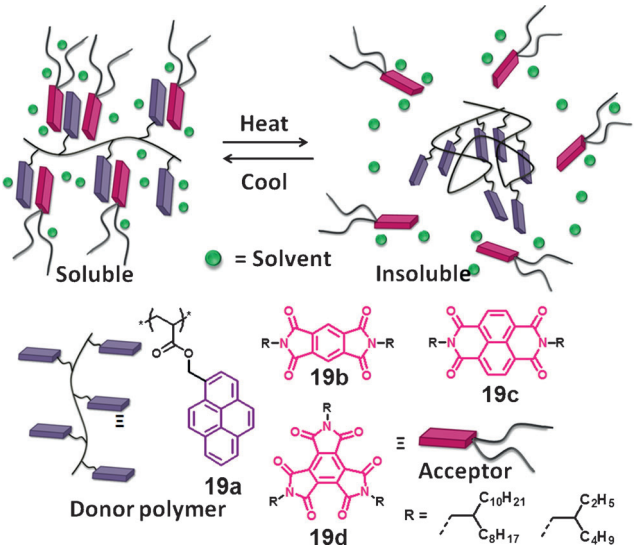


Figure 19. Top: Schematic showing control of polymer phase transition by D–A CT interactions. Bottom: Structure of the donor-containing polymer and various acceptors.

complex becomes soluble. At an elevated temperature, disassembly of the D–A complex thus results in macroscopic precipitation of the polymer and can be assigned as the LCST. As this phenomenon depends on CT complexation, the temperature at which the complex is disintegrated and consequently the LCST can be precisely tuned by varying the structure and concentration of the acceptor units. Noteworthy, the LCST behavior is generally observed for water-soluble polymers, and is governed by the hydrogen bonding between a particular functional group of the polymer and water. In that sense, the present example is conceptually a new one, because it relies upon solubilizing an otherwise insoluble polymer in a given medium by noncovalent complexation with a small molecule that bears the solubilizing group.

D–A alternate stacking interactions has also been utilized to generate supramolecular polymers in solution. Martín and co-workers have shown supramolecular polymerization of an AB-type monomer consisting of a C_{60} acceptor and a bis-(exTTF) donor (Figure 20 A) through CT interactions.[132]

Sessler and co-workers showed that CT interactions mediated the supramolecular polymerization of A2- and B2-type monomers (Figure 20 B) containing TTF donors (**20b–d**) and dinitrophenyl (DNP) acceptors (**20e**) anchored to calyx[4]pyrroles.[133] For **20e**, both *cis* and *trans* isomers (with respect to the positioning of the DNP units) were studied and are not shown in the scheme. Detailed aggregation studies with different combinations of these two types of monomers in $CHCl_3$ reflected the most effective supramolecular polymerization to be that of **20c** and **20e** (*trans*) with a K value of $7.9\times10^5\,\text{M}^{-1}$ and average degree of polymerization (N) of about 90 ($c = 20$ mM), which can be attributed to the combined effect of TTF–DNP CT interactions and pyrrole NH–nitro group hydrogen bonding. They also showed chemoresponsive properties of the polymers in the presence of chloride ion or a stronger acceptor such as trinitrobenzene.

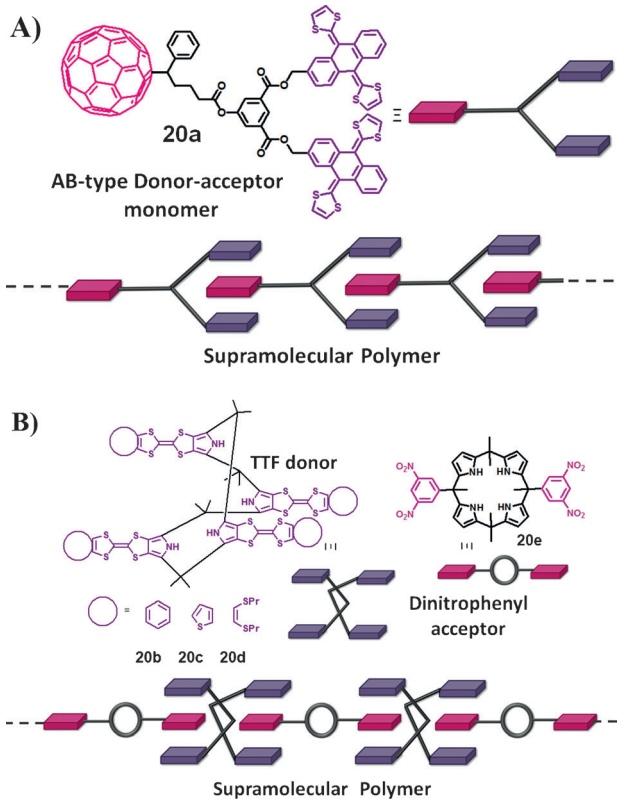


Figure 20. Supramolecular polymers by D–A interactions.

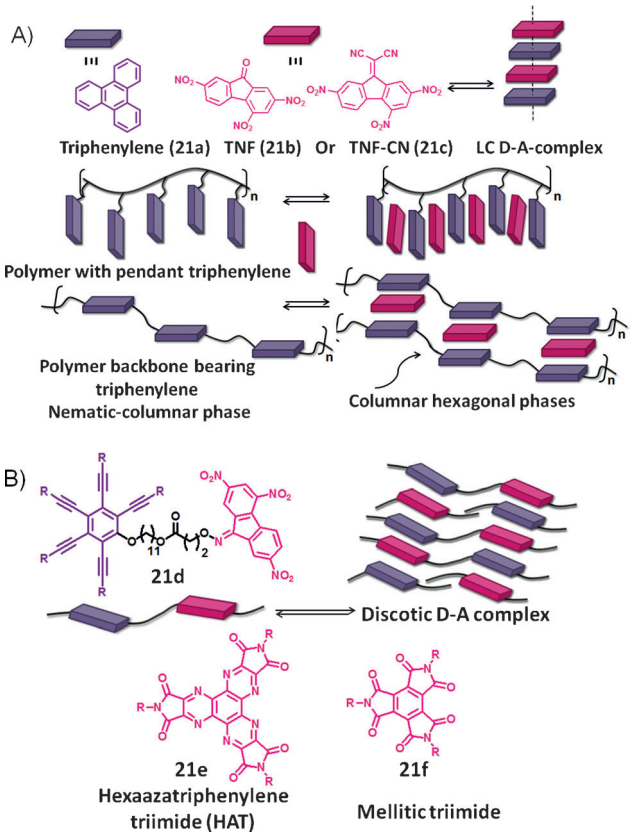


Figure 21. A) Various molecular designs for LC materials derived from a triphenylene donor and TNF acceptor. B) Top: pentakis(phenylethynyl)phenyl–TNF twin molecule that shows LC properties; Bottom: C_3-symmetric acceptors form discotic LC phases with triphenylene based donors.

6. D–A Liquid Crystalline Materials

Alternate D–A stacking has been used as a powerful strategy to achieve thermotropic liquid crystalline (LC) materials.[134] Ringsdorf and co-workers showed CT-complexation-mediated induction of LC phases in otherwise amorphous main-chain and side-chain polymers with triphenylene donors (Figure 21 A) in the presence of aromatic acceptors such as 2,4,7-trinitrofluorenone (TNF) and 2,4,7-trinitrofluoren-9-ylidenemalonodinitrile (TNF-CN).[135] The side-chain and main-chain polymers exhibit nematic-columnar and columnar hexagonal phases in the presence of approxiemtely 25% TNF (**21b**) owing to CT interactions. In the presence of a stronger acceptor, TNF-CN (**21c**), the clearing temperature of the hexagonal phase can be enhanced to about twofold in comparison with that of TNF, thus suggesting not only induction of the mesophases but also modulation of the phase properties are achievable through CT interactions. In subsequent reports, detailed investigations have been carried out on the induction and stabilization of discotic mesophases, transformation of nematic to discotic phases, and evolution of various columnar mesophases by electro-rich triphenylene/alkyl pentakis(phenylethynyl)phenyl ethers based on small molecules (**21d**, Figure 21 B) as well as polymers through CT interactions with TNF, which was either added externally or linked covalently with the donor by different linkers.[136–146]

Subsequently Park, Hamilton, and co-workers showed that C_3-symmetric mellitic triimide (Figure 21 B) could offer a better matching of π surfaces with the triphenylene core to produce more versatile and robust LC phases with the additional advantage of property manipulation using different derivatives, an aspect which was not possible with the TNF acceptor.[147] Chai, Liu, and co-workers introduced[52] another C_3-symmetric acceptor, (Figure 21 B), namely hexaazatriphenylene triimide (HAT), which was found to be even as an acceptor for CT interactions with hexakisalkoxytriphenylene (D11, Scheme 1), as evidenced by a very high association constant ($2.6 \pm 0.8 \times 10^4\,\text{M}^{-1}$) in CH_2Cl_2. They further showed implications of the strong association properties in inducting columnar mesophases by the elongated 1D alternating D–A stacks.

Iverson and co-workers have examined LC properties of various DAN–NDI pairs (Figure 22) as a function of different peripheral alkyl substitutions.[148,149] They showed in most of the D–A pairs, columnar mesophases existed over a wide range of temperature by alternate DAN–NDI stacking and the phase-transition temperatures are directly related to the thermal properties of the individual components and thereby provide a great opportunity of generating mesophases with predictable properties by structural variation of the building blocks. Interestingly they found that depending on the nature of the side chains, a few DAN–NDI pairs exhibited thermoresponsive mesophases to crystalline phase transition, thus resulting in a reorganization from the alternate D–A stacking

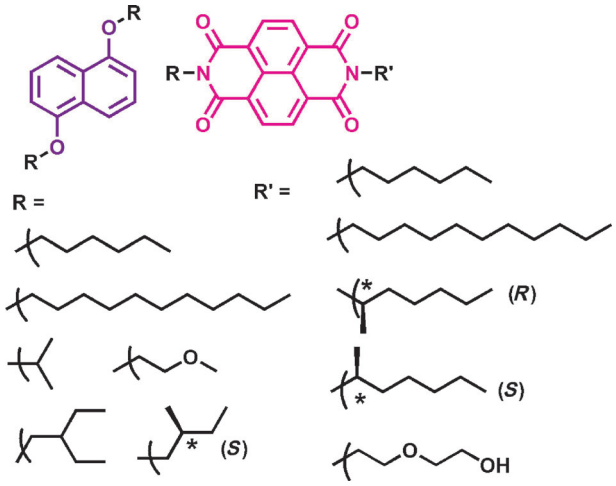


Figure 22. Alkyl chain variations in NDI–DAN LC materials.

to a segregated assembly, (red to yellow color change), which is highly relevant in organic photovoltaics. Reczek and co-workers also elaborately described the influence of the structural variations of NDI- and DAN-based systems for tuning properties of LC phases generated by alternate D–A stacking.[150]

Percec and co-workers have reported[151] an elegant design for mixed supramolecular assembly of D/A-containing polymers and semifluorinated dendrons containing D/A chromophores in the core (Figure 23). They used various commonly

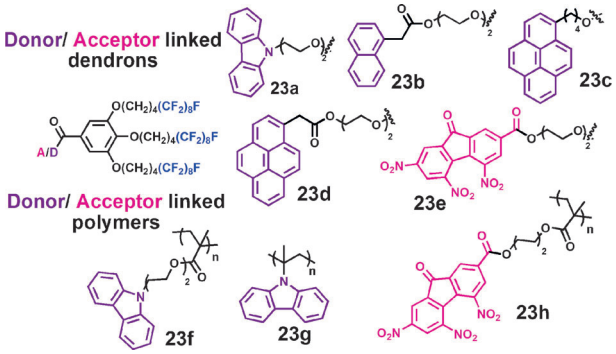


Figure 23. D- and A-containing dendrons and polymers that form columnar co-assembled structures.

used donor and acceptor units such as pyrene, naphthalene, carbazole, and TNF. The linear macromolecules (**23 f**–**h**) form highly stable D–A complexes with the complementary dendrons (**23 a**–**e**) by inter-macromolecule CT interactions, thus producing various supramolecular nanoscale columns with extremely high charge-carrier mobilities. Strong repulsive forces between the peripheral fluorinated chains (shown in blue) of the dendron and the pendant aromatic groups of the linear polymers has been identified as a possible reason for the polymer chains to stay close to the core of the dendron, resulting in a stable co-assembly and consequently high mobility.

7. Outlook

Various weak noncovalent forces play a key role in the assembly of biomolecules. This phenomena has inspired chemists to explore various nonbonding interactions, particularly hydrogen bonding, for the assembly of abiotic systems. However, in last 20 years or so the field of supramolecular chemistry has expanded beyond just hydrogen bonding by employing other noncovalent forces, including π stacking,[9,10] metal–ligand coordination,[15,16] and dipole–dipole interactions.[10] In this article we have shown the utility of the D–A CT interaction, which is not so common in biological systems, in several conceptually different noncovalent molecular designs which produce a diverse range of supramolecular structures. However, even after accumulating all such reports, the number is far less compared to those involving hydrogen bonding possibly because of inherent weak association constants for most of the CT complexes.[27] Nevertheless, D–A complexes can be viewed as being similar to hydrogen bonding in terms of assembly of complementary functional groups with the additional advantages of their easy detection by simple spectroscopic techniques and tolerance to a wide range of solvents. For example, CT complexes with high association constants have been reported in range of solvents including TCE,[80] CH_2Cl_2,[52] $CHCl_3$,[133] $CHCl_3$/MeOH,[110] CH_3CN,[59] and also in protic solvents such as MeOH/H_2O[62] and H_2O.[62] Thus they can be utilized in a much wider domain if supplemented by additional noncovalent forces without losing their complementary nature, as illustrated in this article. The future of this particular strategy depends on how far one can stretch the association strength of complementary building blocks having donor and acceptor units. Currently examples of high association constants (in the range of 10^3–$10^4\,M^{-1}$) for CT complexes are scarce,[52,62,80,94,110,133] even after involving additional nonbonding forces to stabilize the D–A complex. While these are encouraging numbers, they are still three to four orders of magnitude lower when compared to some of the highest *K* values reported for hydrogen bonding,[24] π stacking,[10] or dipolar assemblies.[152] Further enhancement of the binding strengths requires exploration of new materials which account for multiple factors in stabilizing the CT complex as discussed in Section 2 and also designing suitable building blocks decorated with other supramolecular functionalities. Such efforts should be encouraged given the recent reports that suggest alternately stacked D–A systems, if judiciously designed, can be highly promising for organic room-temperature ferroelectrics,[153] photoconductivity,[154] and ambipolar charge transport.[155–159] Thus CT complexes offer exciting future opportunities both in terms of executing elegant structural engineering as well as extracting functional properties for organic electronics.

A.D. acknowledges CSIR, New Delhi, India for a research fellowship. S.G. thanks SERB, New Delhi, India for generous funding (Project: SR/S1/OC-18/2012).

Received: September 3, 2013
Revised: October 18, 2013
Published online: January 21, 2014

[1] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley, New York, **1995**, pp. 139–198.
[2] *Supramolecular Dye Chemistry*, *Topics in Current Chemistry*, *Vol. 258* (Ed.: F. Würthner), Springer, Berlin, **2005**.
[3] R. K. Castellano, J. Rebek, Jr., *J. Am. Chem. Soc.* **1998**, *120*, 3657.
[4] F. Würthner, *Chem. Commun.* **2004**, 1564.
[5] N. Sakai, J. Mareda, E. Vauthey, S. Matile, *Chem. Commun.* **2010**, *46*, 4237.
[6] A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res.* **2007**, *40*, 644.
[7] A. Mishra, C.-Q. Ma, P. Bauerle, *Chem. Rev.* **2009**, *109*, 1141.
[8] M. R. Rao, S.-S. Sun, *Langmuir* **2013**, *29*, 15146.
[9] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491.
[10] Z. Chen, A. Lohr, C. R. Saha-Möller, F. Würthner, *Chem. Soc. Rev.* **2009**, *38*, 564.
[11] T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687.
[12] F. Huang, O. A. Scherman, *Chem. Soc. Rev.* **2012**, *41*, 5879.
[13] G. R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, **1989**.
[14] G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311.
[15] T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* **2013**, *113*, 734.
[16] J. Zhang, C.-Y. Su, *Coord. Chem. Rev.* **2013**, *257*, 1373.
[17] J.-H. Ryu, D.-J. Hong, M. Lee, *Chem. Commun.* **2008**, 1043.
[18] C. A. E. Hauser, S. Zhang, *Chem. Soc. Rev.* **2010**, *39*, 2780.
[19] L. Magginia, D. Bonifazi, *Chem. Soc. Rev.* **2012**, *41*, 211.
[20] B. Rybtchinski, *ACS Nano* **2011**, *5*, 6791.
[21] J. W. Steed, *Chem. Commun.* **2011**, *47*, 1379.
[22] K. P. Milroy, M. H. Sonntag, L. Brunsveld, *Chem. Eur. J.* **2013**, *19*, 10786.
[23] L. J. Prins, D. N. Reinhoudt, P. Timmerman, *Angew. Chem.* **2001**, *113*, 2446; *Angew. Chem. Int. Ed.* **2001**, *40*, 2382.
[24] R. P. Sijbesma, E. W. Meijer, *Chem. Commun.* **2003**, 5.
[25] G. Cooke, V. M. Rotello, *Chem. Soc. Rev.* **2002**, *31*, 275.
[26] D. G. Rodríguez, A. P. H. J. Schenning, *Chem. Mater.* **2011**, *23*, 310.
[27] R. Foster, *Organic Charge-Transfer Complex*, Academic Press, London, **1969**.
[28] R. S. Mulliken, W. B. Person, *Annu. Rev. Phys. Chem.* **1962**, *13*, 107.
[29] S. Shifrin, *Biochim. Biophys. Acta Spec. Sect. Enzymol. Subj.* **1964**, *81*, 205.
[30] H. A. Bent, *Chem. Rev.* **1968**, *68*, 587.
[31] P. Batail, S. J. LaPlaca, J. J. Mayerle, J. B. Torrance, *J. Am. Chem. Soc.* **1981**, *103*, 951.
[32] G. Saito, H. Sasaki, T. Aoki, Y. Yoshida, A. Otsuka, H. Yamochi O. O. Drozdova, K. Yakushi, H. Kitagawa, T. Mitani, *J. Mater. Chem.* **2002**, *12*, 1640.
[33] S. Horiuchi, T. Hasegawa, Y. Tokura, *J. Phys. Soc. Jpn.* **2006**, *75*, 051016.
[34] H. Kuroda, I. Ikemoto, H. Akamatu, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 547.
[35] K. Tahara, T. Fujita, M. Sonoda, M. Shiro, Y. Tobe, *J. Am. Chem. Soc.* **2008**, *130*, 14339.
[36] R. P. Shibaeva, E. B. Yagubskii, *Chem. Rev.* **2004**, *104*, 5347.
[37] J. Lieffrig, O. Jeannin, T. Guizouarn, P. A. -Senzier, M. Fourmigué, *Cryst. Growth Des.* **2012**, *12*, 4248.
[38] T. Murata, Y. Morita, Y. Yakiyama, K. Fukui, H. Yamochi, G. Saito, K. Nakasuji, *J. Am. Chem. Soc.* **2007**, *129*, 10837.
[39] C. A. Hunter, K. R. Lawson, J. Perkins, C. J. Urch, *J. Chem. Soc. Perkin Trans. 2* **2001**, 651.
[40] E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1244; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210.
[41] D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S. Moore, *Chem. Rev.* **2001**, *101*, 3893.
[42] K. K. Kartha, R. D. Mukhopadhyay, A. Ajayaghosh, *Chimia* **2013**, *67*, 51.
[43] S. S. Babu, S. Prasanthkumar, A. Ajayaghosh, *Angew. Chem.* **2012**, *124*, 1800; *Angew. Chem. Int. Ed.* **2012**, *51*, 1766.
[44] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725.
[45] V. Balzani, M. Gómez-López, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405.
[46] C. O. Dietrich-Buchecker, J. P. Sauvage, *Chem. Rev.* **1987**, *87*, 795.
[47] X. Ma, H. Tian, *Chem. Soc. Rev.* **2010**, *39*, 70.
[48] S. F. M. van Dongen, S. Cantekin, J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *Chem. Soc. Rev.* **2014**, *43*, 99.
[49] Y. H. Ko, E. Kim, I. Hwang, K. Kim, *Chem. Commun.* **2007**, 1305.
[50] M. B. Nielsen, C. Lomholt, J. Becher, *Chem. Soc. Rev.* **2000**, *29*, 153.
[51] J. Ferraris, D. O. Cowan, V. V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948.
[52] L. M. Klivansky, D. Hanifi, G. Koshkakaryan, D. R. Holycross, E. K. Gorski, Q. Wu, M. Chai, Y. Liu, *Chem. Sci.* **2012**, *3*, 2009.
[53] J.-Y. Wang, J. Yan, L. Ding, Y. Ma, J. Pei, *Adv. Funct. Mater.* **2009**, *19*, 1746.
[54] A. J. Zych, B. L. Iverson, *J. Am. Chem. Soc.* **2000**, *122*, 8898.
[55] K. Medjanik, D. Kutnyakhov, S. A. Nepijko, G. Schönhense, S. Naghavi, V. Alijani, C. Felser, N. Koch, R. Rieger, M. Baumgartend, K. Müllen, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7184.
[56] G. Briegleb, *Elektronen-Donor-Acceptor-Komplexe*, Springer, Berlin, **1961**.
[57] H. M. Colquhoun, E. P. Goodings, J. M. Maud, J. F. Stoddart, J. B. Wolstenholme, J. D. Williams, *J. Chem. Soc. Perkin Trans. 2* **1985**, 607.
[58] R. Foster, *J. Chem. Soc.* **1960**, 1075.
[59] M. B. Nielsen, J. O. Jeppesen, J. Lau, C. Lomholt, D. Damgaard, J. P. Jacobsen, J. Becher, J. F. Stoddart, *J. Org. Chem.* **2001**, *66*, 3559.
[60] Q.-Z. Zhou, M.-X. Jia, X.-B. Shao, L.-Z. Wu, X.-K. Jiang, Z.-T. Lia, G.-J. Chen, *Tetrahedron* **2005**, *61*, 7117.
[61] N. S. S. Kumar, M. D. Gujrati, J. N. Wilson, *Chem. Commun.* **2010**, *46*, 5464.
[62] M. S. Cubberley, B. L. Iverson, *J. Am. Chem. Soc.* **2001**, *123*, 7560.
[63] D. B. Smithrud, F. Diederich, *J. Am. Chem. Soc.* **1990**, *112*, 339.
[64] Z. Chen, B. Fimmela, F. Würthner, *Org. Biomol. Chem.* **2012**, *10*, 5845.
[65] L. A. Estroff, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201.
[66] N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821.
[67] P. Dastidar, *Chem. Soc. Rev.* **2008**, *37*, 2699.
[68] L. E. Buerkle, S. J. Rowan, *Chem. Soc. Rev.* **2012**, *41*, 6089.
[69] U. Maitra, P. V. Kumar, N. Chandra, L. J. D'Souza, M. D. Prasanna, A. R. Raju, *Chem. Commun.* **1999**, 595.
[70] P. Babu, N. M. Sangeetha, P. Vijaykumar, U. Maitra, K. Rissanen, A. R. Raju, *Chem. Eur. J.* **2003**, *9*, 1922.
[71] R. K. Das, S. Banerjee, G. Raffy, A. D. Guerzo, J.-P. Desvergne, U. Maitra, *J. Mater. Chem.* **2010**, *20*, 7227.
[72] R. Kandanelli, U. Maitra, *Photochem. Photobiol. Sci.* **2012**, *11*, 1724.
[73] B. G. Bag, G. C. Maity, S. K. Dinda, *Org. Lett.* **2006**, *8*, 5457.
[74] D. Rizkov, J. Gun, O. Lev, R. Sicsic, A. Melman, *Langmuir* **2005**, *21*, 12130.
[75] C. Wang, D. Zang, D. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 17372.
[76] Y. Liu, N. Zheng, H. Li, B. Yin, *Soft Matter* **2013**, *9*, 5261.
[77] X. Mei, J. Ouyang, *Langmuir* **2011**, *27*, 10953.
[78] J. R. Moffat, D. K. Smith, *Chem. Commun.* **2008**, 2248.

[79] A. Das, M. R. Molla, A. Banerjee, A. Paul, S. Ghosh, *Chem. Eur. J.* **2011**, *17*, 6061.
[80] A. Das, M. R. Molla, B. Maity, D. Koley, S. Ghosh, *Chem. Eur. J.* **2012**, *18*, 9849.
[81] For a recent review on self-sorting see: M. M. Safont-Sempere, G. Fernández, F. Würthner, *Chem. Rev.* **2011**, *111*, 5784.
[82] M. R. Molla, A. Das, S. Ghosh, *Chem. Eur. J.* **2010**, *16*, 10084.
[83] D. F. Evans, H. Wennerstrom, *The Colloidal Domain*, 2nd ed., Wiley-VCH, New York, **1999**.
[84] R. K. O'Reilly, C. J. Hawker, K. L. Wooley, X. Zhang, C. Wang, *Chem. Soc. Rev.* **2011**, *40*, 94.
[85] X. Zhang, C. Wang, *Chem. Soc. Rev.* **2011**, *40*, 94.
[86] C. Wang, Z. Q. Wang, X. Zhang, *Acc. Chem. Res.* **2012**, *45*, 608.
[87] C. Wang, S. Yin, S. Chen, H. Xu, Z. Wang, X. Zhang, *Angew. Chem.* **2008**, *120*, 9189; *Angew. Chem. Int. Ed.* **2008**, *47*, 9049.
[88] C. Wang, Y. Guo, Y. Wang, H. Xu, R. Wang, X. Zhang, *Angew. Chem.* **2009**, *121*, 9124; *Angew. Chem. Int. Ed.* **2009**, *48*, 8962.
[89] C. Wang, Y. Guo, Z. Wang, X. Zhang, *Langmuir* **2010**, *26*, 14509.
[90] K. V. Rao, K. Jayaramulu, T. K. Maji, S. J. George, *Angew. Chem.* **2010**, *122*, 4314; *Angew. Chem. Int. Ed.* **2010**, *49*, 4218.
[91] K. V. Rao, S. J. George, *Chem. Eur. J.* **2012**, *18*, 14286.
[92] K. Liu, C. Wang, Z. Li, X. Zhang, *Angew. Chem.* **2011**, *123*, 5054; *Angew. Chem. Int. Ed.* **2011**, *50*, 4952.
[93] K. Liu, Y. Yao, Y. Liu, C. Wang, Z. Li, X. Zhang, *Langmuir* **2012**, *28*, 10697.
[94] M. R. Molla, S. Ghosh, *Chem. Eur. J.* **2012**, *18*, 9860.
[95] H. T. McMahon, J. L. Gallop, *Nature* **2005**, *438*, 590.
[96] S. H. Gellman, *Acc. Chem. Res.* **1998**, *31*, 173.
[97] C. Schmuck, *Angew. Chem.* **2003**, *115*, 2552; *Angew. Chem. Int. Ed.* **2003**, *42*, 2448.
[98] G. Guichard, I. Huc, *Chem. Commun.* **2011**, *47*, 5933.
[99] D. W. Zhang, X. Zhao, J. L. Hou, Z. T. Li, *Chem. Rev.* **2012**, *112*, 5271.
[100] R. S. Lokey, B. L. Iverson, *Nature* **1995**, *375*, 303.
[101] J. Q. Nguyen, B. L. Iverson, *J. Am. Chem. Soc.* **1999**, *121*, 2639.
[102] C. Peebles, R. Piland, B. L. Iverson, *Chem. Eur. J.* **2013**, *19*, 11598.
[103] V. J. Bradford, B. L. Iverson, *J. Am. Chem. Soc.* **2008**, *130*, 1517.
[104] G. J. Gabriel, S. Orey, B. L. Iverson, *J. Am. Chem. Soc.* **2005**, *127*, 2637.
[105] G. J. Gabriel, B. L. Iverson, *J. Am. Chem. Soc.* **2002**, *124*, 15174.
[106] X. Zhao, M.-X. Jia, X.-K. Jiang, L.-Z. Wu, Z.-T. Li, G.-J. Chen, *J. Org. Chem.* **2004**, *69*, 270.
[107] S. Ghosh, S. Ramakrishnan, *Angew. Chem.* **2004**, *116*, 3326; *Angew. Chem. Int. Ed.* **2004**, *43*, 3264.
[108] S. Ghosh, S. Ramakrishnan, *Macromolecules* **2005**, *38*, 676.
[109] S. Ghosh, S. Ramakrishnan, *Angew. Chem.* **2005**, *117*, 5577; *Angew. Chem. Int. Ed.* **2005**, *44*, 5441.
[110] S. De, D. Koley, S. Ramakrishnan, *Macromolecules* **2010**, *43*, 3183.
[111] S. G. Ramkumar, S. Ramakrishnan, *Macromolecules* **2010**, *43*, 2307.
[112] S. De, S. Ramakrishnan, *Macromolecules* **2009**, *42*, 8599.
[113] S. De, S. Ramakrishnan, *Chem. Asian J.* **2011**, *6*, 149.
[114] S. G. Ramkumar, S. Ramakrishnan, *J. Chem. Sci.* **2008**, *120*, 187.
[115] K. Jalani, M. Kumar, S. J. George, *Chem. Commun.* **2013**, *49*, 5174.
[116] W. D. Gill, *J. Appl. Phys.* **1972**, *43*, 5033.
[117] S. R. Turner, C. Auclair, *Macromolecules* **1976**, *9*, 868.
[118] S. R. Turner, *Macromolecules* **1980**, *13*, 782.
[119] J. M. R. Parade, V. Percec, *Macromolecules* **1986**, *19*, 55.
[120] F. Ilhan, M. Gray, K. Blanchette, V. M. Rotello, *Macromolecules* **1999**, *32*, 6159.
[121] A. F. M. Kilbinger, R. H. Grubbs, *Angew. Chem.* **2002**, *114*, 1633; *Angew. Chem. Int. Ed.* **2002**, *41*, 1563.
[122] J. J. Reczek, B. L. Iverson, *Macromolecules* **2006**, *39*, 5601.
[123] J. Romulus, S. Patel, M. Weck, *Macromolecules* **2012**, *45*, 70.
[124] Ref. [61].
[125] H. M. Colquhoun, Z. Zhu, D. J. Williams, *Org. Lett.* **2003**, *5*, 4353.
[126] H. M. Colquhoun, Z. Zhu, *Angew. Chem.* **2004**, *116*, 5150; *Angew. Chem. Int. Ed.* **2004**, *43*, 5040.
[127] H. M. Colquhoun, Z. Zhu, C. J. Cardin, Y. Gan, *Chem. Commun.* **2004**, 2650.
[128] H. M. Colquhoun, Z. Zhu, C. J. Cardin, Y. Gan, M. G. B. Drew, *J. Am. Chem. Soc.* **2007**, *129*, 16163.
[129] S. Burattini, H. M. Colquhoun, J. D. Fox, D. Friedmann, B. W. Greenland, P. J. F. Harris, W. Hayes, M. E. Mackay, S. J. Rowan, *Chem. Commun.* **2009**, 6717.
[130] S. Burattini, B. W. Greenland, W. Hayes, M. E. Mackay, S. J. Rowan, H. M. Colquhoun, *Chem. Mater.* **2011**, *23*, 6.
[131] S. Amemori, K. Kokado, K. Sada, *Angew. Chem.* **2013**, *125*, 4268; *Angew. Chem. Int. Ed.* **2013**, *52*, 4174.
[132] G. Fernández, E. M. Pérez, L. Sánchez, N. Martín, *Angew. Chem.* **2008**, *120*, 1110; *Angew. Chem. Int. Ed.* **2008**, *47*, 1094.
[133] J. S. Parka, K. Y. Yoonb, D. S. Kima, V. M. Lyncha, C. W. Bielawskia, K. P. Johnstonb, J. L. Sessler, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 20913.
[134] K. Praefcke, D. Singer in *Handbook of Liquid Crystals*, *Vol. 2B* (Eds.: D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vills), Wiley-VCH, Weinheim, **1998**, p. 945.
[135] H. Ringsdorf, R. Wüstefeld, E. Zerta, M. Ebert, J. H. Wendorff, *Angew. Chem.* **1989**, *101*, 934; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 914.
[136] M. Ebert, G. Frick, C. Baher, J. H. Wendorff, R. Wüstefeld, H. Ringsdorf, *Liq. Cryst.* **1992**, *11*, 293.
[137] H. Bengs, M. Ebert, O. Karthaus, B. Kohne, K. Praefcke, H. Ringsdorf, J. H. Wendorff, R. Wüstefeld, *Adv. Mater.* **1990**, *2*, 141.
[138] V. V. Tsukruk, J. H. Wendorff, *Langmuir* **1993**, *9*, 614.
[139] W. Kranig, C. Boeffel, H. W. Spiess, O. Karathaus, H. Ringsdorf, R. Wüstefeld, *Liq. Cryst.* **1990**, *8*, 375.
[140] M. Möller, V. Tsukruk, J. H. Wendorff, H. Bengs, H. Ringsdorf, *Liq. Cryst.* **1992**, *12*, 17.
[141] D. Janietz, K. Praefcke, D. Singer, *Liq. Cryst.* **1993**, *13*, 247.
[142] K. Praefcke, D. Singer, B. Kohne, M. Ebert, A. Liebmann, J. H. Wendorff, *Liq. Cryst.* **1991**, *10*, 147.
[143] K. Praefcke, D. Singer, M. Langner, B. Kohne, M. Ebert, A. Liebmann, J. H. Wendorff, *Mol. Cryst. Liq. Cryst.* **1991**, *215*, 121.
[144] D. Janietz, *Chem. Commun.* **1996**, 713.
[145] S. Mahlstedt, D. Janietz, C. Schmidt, A. Stracke, J. H. Wendorff, *Liq. Cryst.* **1999**, *26*, 1359.
[146] S. Mahlstedt, D. Janietz, A. Stracke, J. H. Wendorff, *Chem. Commun.* **2000**, 1.
[147] L. Y. Park, D. G. Hamilton, E. A. McGehee, K. A. McMenimen, *J. Am. Chem. Soc.* **2003**, *125*, 10586.
[148] J. J. Reczek, K. R. Villazor, V. Lynch, T. M. Swager, B. L. Iverson, *J. Am. Chem. Soc.* **2006**, *128*, 7995.
[149] P. M. Alvey, J. J. Reczek, V. Lynch, B. L. Iverson, *J. Org. Chem.* **2010**, *75*, 7682.
[150] K. R. Leight, B. E. Esarey, A. E. Murray, J. J. Reczek, *Chem. Mater.* **2012**, *24*, 3318.
[151] V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson, H. Duan, *Nature* **2002**, *417*, 384.
[152] F. Würthner, S. Yao, T. Debaerdemaeker, R. Wortmann, *J. Am. Chem. Soc.* **2002**, *124*, 9431.
[153] A. S. Tayi, A. K. Shveyd, A. C.-H. Sue, J. M. Szarko, B. S. Rolczynski, D. Cao, T. J. Kennedy, A. Sarjeant, C. L. Stern, W. F. Paxton, W. Wu, S. K. Dey, A. C. Fahrenbach, J. R. Guest,

H. Mohseni, L. X. Chen, K. L. Wang, J. F. Stoddart, S. I. Stupp, *Nature* **2012**, *488*, 485.
[154] J. Luo, L. Chen, J.-Y. Wang, T. Lei, L.-Y. Li, J. Pei, Y. Song, *New J. Chem.* **2010**, *34*, 2530.
[155] S. Horiuchi, Y. Tokura, *Nat. Mater.* **2008**, *7*, 357.
[156] J. J. Tan, Z. Ma, W. Xu, G. Zhao, H. Geng, C. Di, W. Hu, Z. Shuai, K. Singh, D. Zhu, *J. Am. Chem. Soc.* **2013**, *135*, 558.
[157] J. Zhang, H. Geng, T. S. Virk, Y. Zhao, J. Tan, C.-a. Di, W. Xu, K. Singh, W. Hu, Z. Shuai, Y. Liu, D. Zhu, *Adv. Mater.* **2012**, *24*, 2603.
[158] S. K. Park, S. Varghese, J. H. Kim, S.-J. Yoon, O. K. Kwon, B.-K. An, J. Gierschner, S. Y. Park, *J. Am. Chem. Soc.* **2013**, *135*, 4757.
[159] A. A. Sagade, K. V. Rao, S. J. George, A. Datta, G. U. Kulkarni, *Chem. Commun.* **2013**, *49*, 5847.