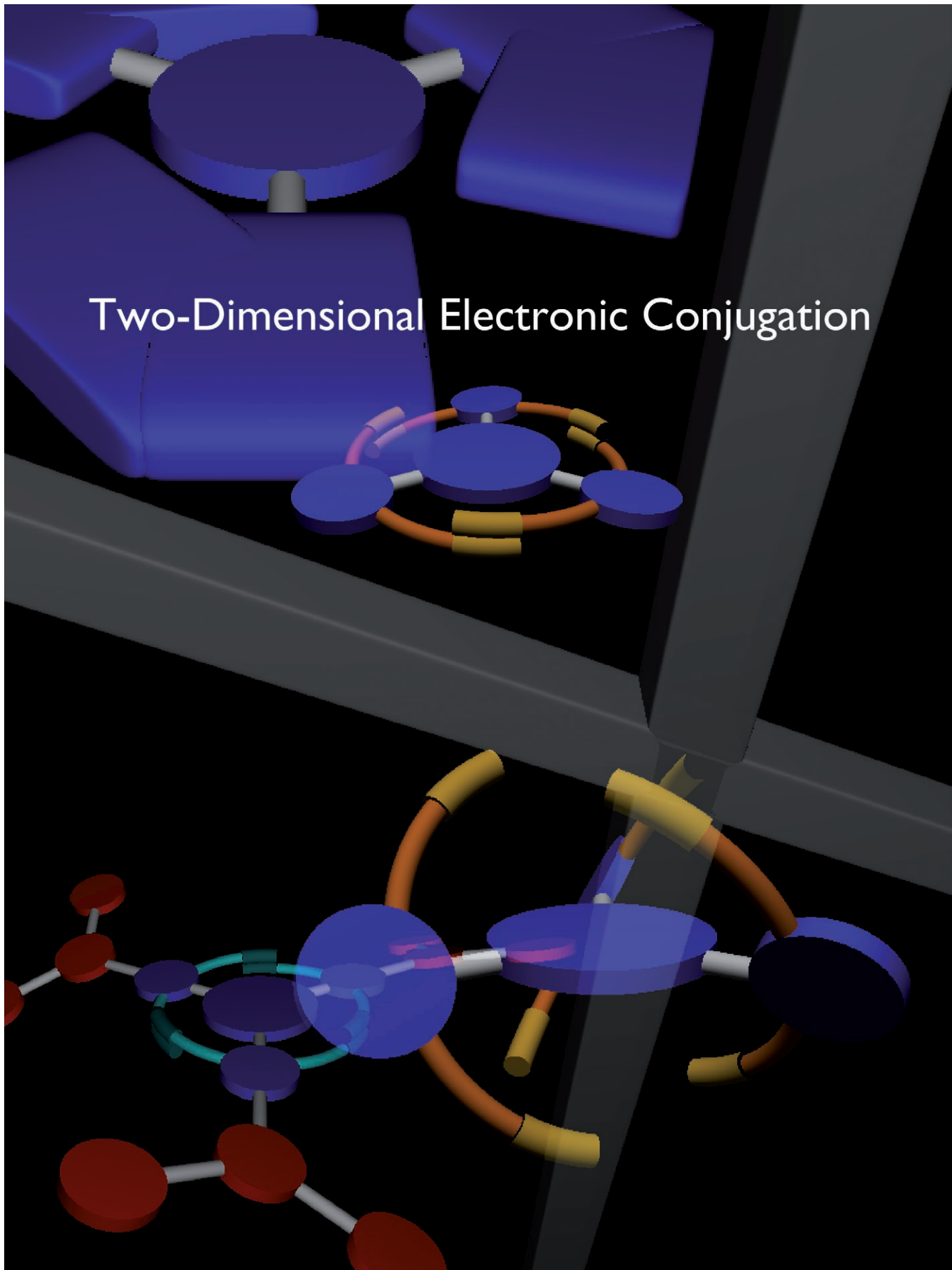Two-Dimensional Electronic Conjugation

Two-Dimensional Electronic Conjugation: Statics and Dynamics at Structural Domains Beyond Molecular Wires

## Elizabeth Opsitnick and Dongwhan Lee*[a]

Abstract: Chemical architectures supporting a high degree of electronic conjugation serve as important functional components in devices and materials for advanced electronic and photonic applications. Increasing the spatial dimensionality of such constructs can fundamentally modify their optoelectronic properties and significantly alter intra- and intermolecular interactions that are crucial for understanding and controlling charge/energy-transfer processes. In this article, emerging design principles in the construction of well-defined conjugated platforms beyond molecular wires are highlighted. Both covalent and noncovalent approaches can be strategically employed to position one-dimensional (1D) substructures in a spatially well-defined manner in order to enhance both structural and functional complexity in a two-dimensional (2D) setting. A predictable and controllable switching mechanism can be designed and implemented with mobile 2D electronic conjugation that operates by correlated motions of inherently rigid 1D subunits. This emerging "dynamic" approach complements and challenges the prevailing "static" paradigm of conjugated chemical architectures.

Keywords: conjugation · cooperative effects · molecular devices · pi interactions · switching

Introduction

Design of molecular platforms facilitating electronic conjugation continues to be an engaging challenge. Since the seminal discovery of doped polyacetylenes as structurally flexible and synthetically modifiable surrogates of conventional conducting and semiconducting materials,[1,2] linearly π-conjugated organic structures have emerged as an important class of functional organic materials (Scheme 1).[3–6] The
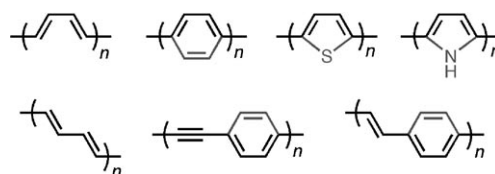
Scheme 1. Representative 1D conjugation comprised of repeating units that formally trace the backbone structures of *cis*-polyacetylenes, *trans*-polyacetylenes, or their hybrids.

structure–property relationships dictating such linearly conjugated platforms have often been rationalized by invoking the concept of a one-dimensional (1D) "molecular wire" that functions as an effective conduit for charge and/or energy carriers.[7,8]

Within this context, two-dimensional (2D) electronic conjugation can be broadly defined as rational molecular designs and innovative synthetic efforts to build electronically conjugated platforms beyond the 1D confinements of molecular wires. As will be discussed in the following sections, increases in the spatial dimensionality of the 1D electronic conjugation not only expand the space sampled by delocalized charge/energy carriers, but also introduce orientational factors dictating electronic interactions between segmented 1D subunits. Additionally, the periphery of radially expanded electronic conjugation can be functionalized to guide self-assembly of planar building blocks and drive the structural folding and unfolding motions that can fundamentally modify the photophysical properties associated with 2D conjugation.

State-of-the-Art 2D Conjugation: Cruciforms, Dendrimers, and Graphitic Discs

Cross-linking is one intuitive approach to increase the spatial dimensionality of 1D conjugation.[9] As shown in

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Scheme 2, an essentially perpendicular disposition of linear π strands should automatically generate minimal 2D structures that can be best modeled with cruciforms **1–3** or [2.2]paracyclophane-fused double-decker-type structures **4**.
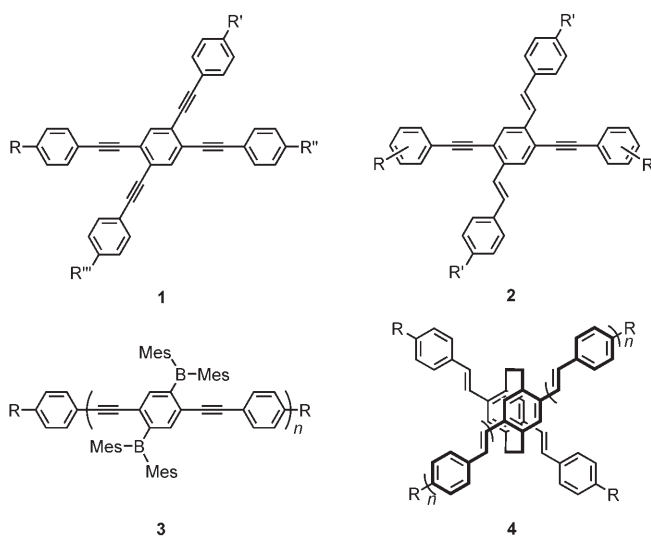

Scheme 2. 2D conjugation constructed by cross-linking of 1D phenyleneethynylene, phenylenevinylene, or bis(diarylboryl)phenylene segments.

Depending on the substitution pattern, the HOMO and LUMO associated with these prototypical cross-conjugated architectures can be localized to each individual 1D strand or delocalized over the entire molecule.[10–12] This unusual property enabled independent electronic control of the band gap and intramolecular charge-transfer (ICT) pathways within the 2D framework. A conceptually related cruciform **3** exploits p–π interactions between the π-conjugated phenyleneethynylene units and the cross-conjugated bulky boryl groups supplying empty p orbitals.[12] Similarly to **2**, the HOMO and LUMO of **3** are orthogonally disposed, thereby facilitating ICT and strong luminescence with large Stokes shifts.

A topologically related double-decker-type **4**, a variant of the cruciform, can be constructed using a [2.2]paracyclophane unit as a branching point.[13] The layered geometry with a short intra-annular distance (ca. 3.1 Å) brings two π-extended segments into close proximity and encourages through-space electronic interactions between 1D subunits.[14] Notably, the rigid [2.2]paracyclophane juncture establishes a precise orientational relationship between the two linearly extended chromophores that give rise to electronic states which are either localized on individual 1D strands or delocalized through transannular interactions. These examples elegantly demonstrate how a precise spatial control over the electronic structures can directly impact the photophysical properties of 2D cross-conjugation by through-bond or through-space interactions.

Hyperbranching of segmented 1D structural motifs can further facilitate the construction of 2D conjugation. The nonlinear growth strategy typically employed in the synthesis of dendritic structures (Scheme 3) rapidly builds up topological and functional complexity in a relatively short sequence of synthetic operations.[15, 16] Understandably, advances in transition-metal-catalyzed cross-coupling protocols
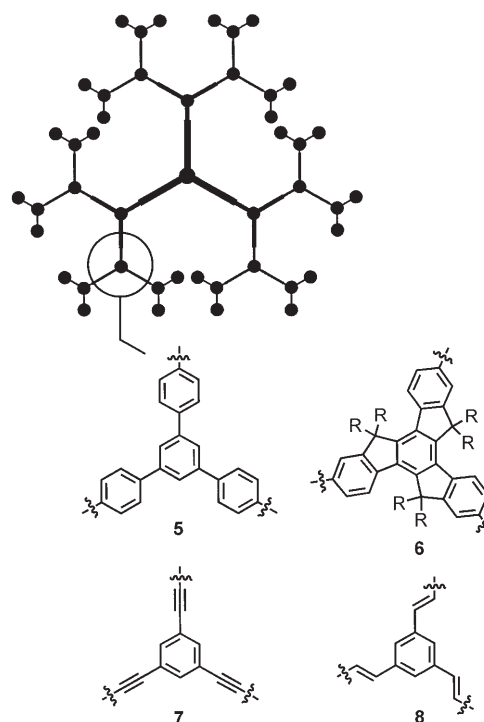

Scheme 3. Schematic representation of dendritic 2D conjugation and its representative building blocks derived from phenylene (**5**), truxene (**6**), phenyleneethynylene (**7**), and phenylenevinylene (**8**).

have significantly contributed to the development of high-yielding routes to dendritic structures through repetitive C−C bond formation,[17] essentially revolutionizing the scope of readily accessible hyperbranched π-conjugated structures.

As shown in Scheme 3, dendritic 2D conjugation can be constructed with phenylene-,[18] phenyleneethynylene-,[15,19,20] or phenylenevinylene-derived[21] building blocks. Truxenes are ring-fused analogues of hyperbranched phenylenes that should suffer less from structural distortion when integrated into dendritic platforms.[22] Oligomeric phenyleneethynylenes have also been used extensively to construct shape-persistent macrocycles, which represent another important class of planar conjugated systems.[15, 23]

These rigid building blocks are ideal for positioning multiple chromophores with precise distance and orientation relationships. Electronic interactions between spatially well-defined locations within such 2D systems facilitate directional transfer of excited-state energy.[24,25] In addition to providing a synthetic handle to tune the excited-state energy level as a function of conjugation length, the shape-persistent nature of the π-conjugation pathways plays a pivotal role by minimizing conformational disorder and preventing undesired energy dissipation through thermal motions.

A complete planarization and full electron delocalization of hyperbranched 2D conjugation eventually leads to graphite-like chemical architectures (Scheme 4). Peri-condensed polycyclic aromatic hydrocarbons are representative mem-
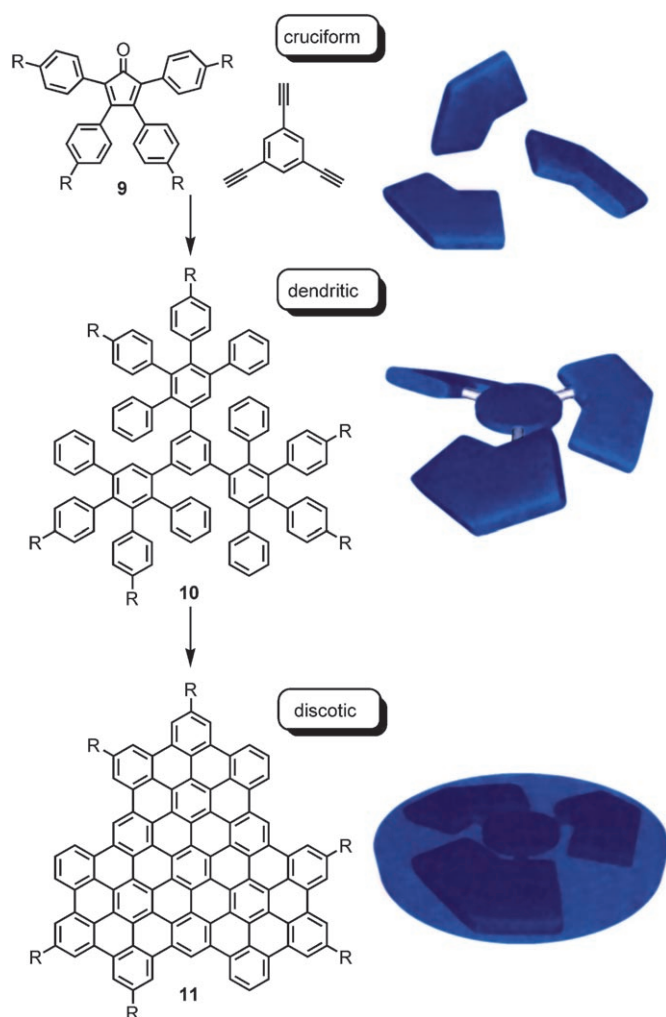

Scheme 4. Structural "evolution" of 2D conjugation, in which cross-linked 1D conjugated segments (**9**) were brought together to furnish a dendritic architecture (**10**), which was subsequently stitched to furnish a fully ring-fused graphitic disc (**11**).[28] Shown next to the synthetic scheme is a schematic representation of the conceptual linkage between cruciform, dendrimer, and superbenzene.

bers of such "superbenzenes",[26] the highly symmetric core of which provides large π surfaces that self-assemble to organized columnar stacks ideal for charge transport.[27,28] Synthetic routes to radially expanded **11**, for example, require covalent pre-assembly of its dendritic precursor **10** and its subsequent dehydrohalogenation to connect adjacent aryl segments.[29] This synthetic sequence nicely parallels the concept map (Scheme 4) relating the cruciform, dendrimer, and graphitic discs as an emerging family of 2D-conjugated structures.

Dynamic 2D Conjugation: Escape from the Molecular Flatland

Structural distortion of conjugation pathways can significantly alter their electronic properties. For this reason, geometrically nonplanar π conjugation has attracted significant attention from both theoretical and synthetic chemistry communities.[30] Representative small molecule examples presenting curved 2D surfaces include paracyclophanes,[14] twisted acenes,[31] arenes,[32] and bridged annulenes.[33] Unlike their planar benzenoid analogues maintaining flat 2D surfaces, these bowl-shaped systems can potentially undergo dynamic structural transformation between the curved and planar geometry. If such structural interconversion can be externally triggered and the accompanying changes in electronic properties can be conveniently monitored, this dynamic 2D conjugation promises enormous opportunities for switching and actuation.[34]

Corannulenes (**12**) are truncated segments of fullerenes and have curved surfaces, which undergo constant inversion motions (Scheme 5).[32,35] Variable-temperature ^{1}H NMR
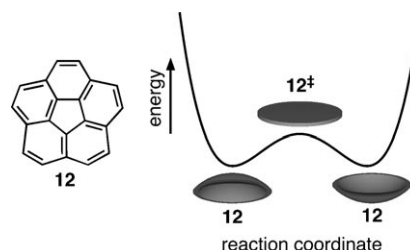

Scheme 5. Interconversion between the curved (**12**) and planar (**12**$^+$) 2D conjugation of corannulene.[36]

studies of a series of substituted **12** revealed details of this process proceeding through the transition state **12**$^+$ with an energy barrier of ≈11.5 kcal mol^{-1}.[36] This "conformational switching" between planar and curved 2D conjugation is conceptually intriguing, but the transient nature of **12**$^+$ renders this mode of operation practically less relevant.

## Switchable 2D Conjugation: Mode of Operation

One viable strategy to reversibly distort 2D conjugation pathways is depicted in Scheme 6. A dendritic molecular prototype **13** can be envisioned in which three peripheral aromatic groups are connected to a common C_3-symmetric molecular core that is electronically conjugated to each branch. As such, rotational motions about each of the three single bonds that connect radially disposed subunits can control the degree of overlap between adjacent p orbitals as a function of the dihedral angles (τ_n; $n=1$–3), with maximum conjugation at $\tau_n=0°$ (eclipsed) and complete deconjugation at $\tau_n=90°$ (orthogonal). A simple geometrical consideration dictates that the collective effects of such individual pairwise interactions can be maximized only when the three torsional
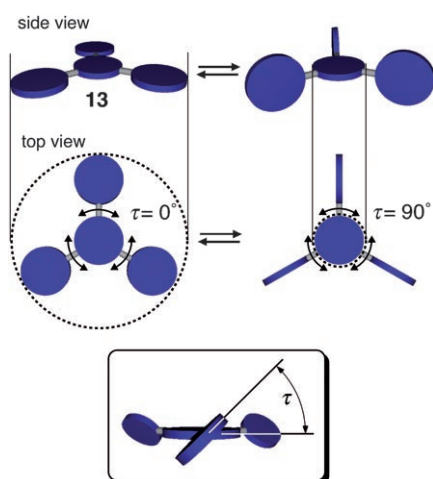
Scheme 6. Conformational switching of a prototypical 2D conjugation **13**. Blue discs are arbitrary arylene-extended subunits; dotted circles define conjugation area. The dihedral angle τ measures deviation of the peripheral aryl groups from the molecular core. Correlated tilting motions of the peripheral discs can interconvert the fully conjugated ($\tau = 0°$) and completely deconjugated ($\tau = 90°$) conformations of **13**, which correspond to the maximum expansion and shrinkage of the conjugation area, respectively.

motions are correlated, that is, $\tau_1 = \tau_2 = \tau_3 = \tau$. With τ varied between 0° to 90°, compound **13** should experience systematic expansion and shrinkage of its effective *conjugation area* as defined in Scheme 6.

Conceptually intuitive and operationally simple as it might appear, correlating rotational motions at multiple nonproximate locations within this inherently flexible structure is a formidable synthetic task. A genuine appreciation of the level of challenge here can be obtained when a direct comparison is made with the linear counterpart of **13** comprising an identical number of mobile components. As shown in Scheme 7, changes in the overall conjugation length in this "particle-in-a-1D-box" **14** require torsional motions about just one single bond. This is exemplified by functionalized biphenyls **15–17**,[37] in which conformational restrictions can fundamentally modify the photophysical
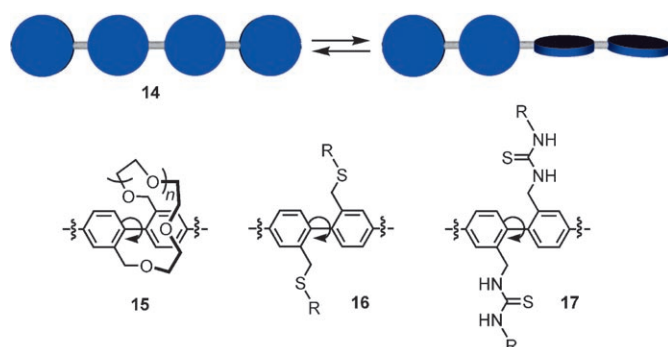
Scheme 7. Reversible conformational switching of a linear conjugation **14** through rotation about a single bond. Biphenyl-derived structures **15–17** have functional groups that can reversibly interact with guest species to control the degree of this torsional twisting, shown by the curved arrows.

properties of dynamic 1D conjugation. The imminent question is whether this idea can be taken to the next level for the 2D system shown in Scheme 6.

Correlating Molecular Motions

Uncontrolled internal torsional motions of **13** would give rise to an ensemble of conformations (Figure 1) and popula-
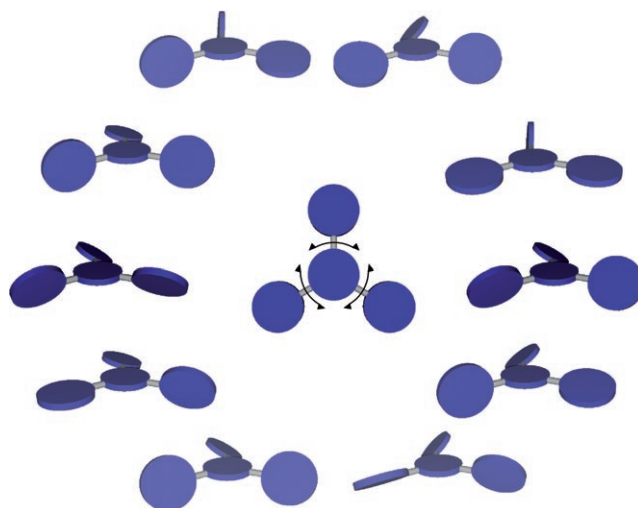

Figure 1. Schematic representation of an ensemble of conformers of **13** resulting from uncorrelated tilting motions ($\tau_1 \neq \tau_2 \neq \tau_3$).

tion-averaged properties that are difficult to understand and control. A tight mechanical coupling scheme is thus desired that can correlate tilting motions of multiple aromatic units and thereby minimize the conformational inhomogeneity (Scheme 6).

Shape-adaptive C_3-symmetric molecules **18a–c** served as a
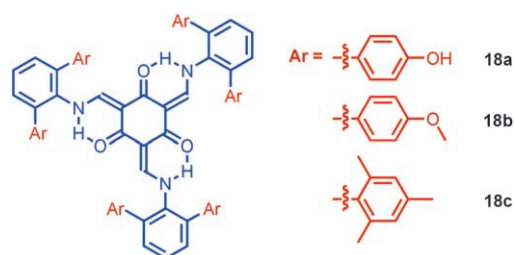
useful structural template to implement controllable dynamic properties to 2D conjugation. These sterically congested biconcave structures were initially designed to switch between the unfolded (**19**) and folded (**20** and **20′**) conformations through iris-like opening and closing motions (Scheme 8).[38] Specifically, close van der Waals contacts between adjacent bulky aromatic "wing" units in **18a–c** dictate that tilting motions around the pivotal C−C bonds should proceed in a merry-go-round fashion to furnish the flattened conformers **20** or **20′**. Uncorrelated tilting such as **21** would
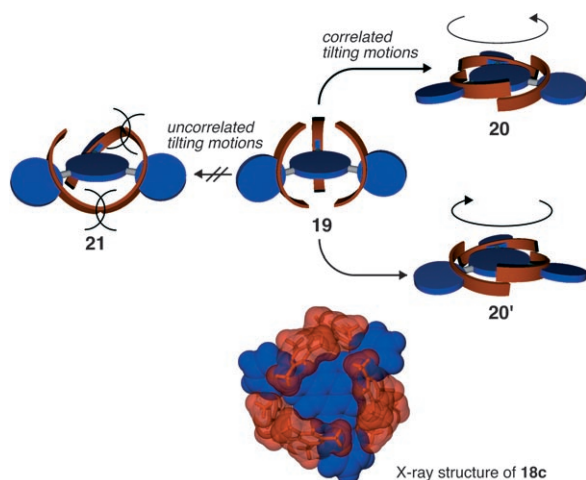
Scheme 8. Structural folding of a C_3-symmetric biconcave structure **19** proceeds by concerted tilting of three peripheral *m*-terphenyl groups. An enantiomeric pair of folded conformers **20** and **21′** are obtained depending on the absolute directionality of correlated C−C bond rotations, which are amplified and translated to global conformational switching. Shown below is the solid-state structure of **18c** generated using X-ray coordinates, in which the tris(*N*-salicylideneaniline) core and 2,6-dimesityl substituents are color-coded in blue and red, respectively.[28]
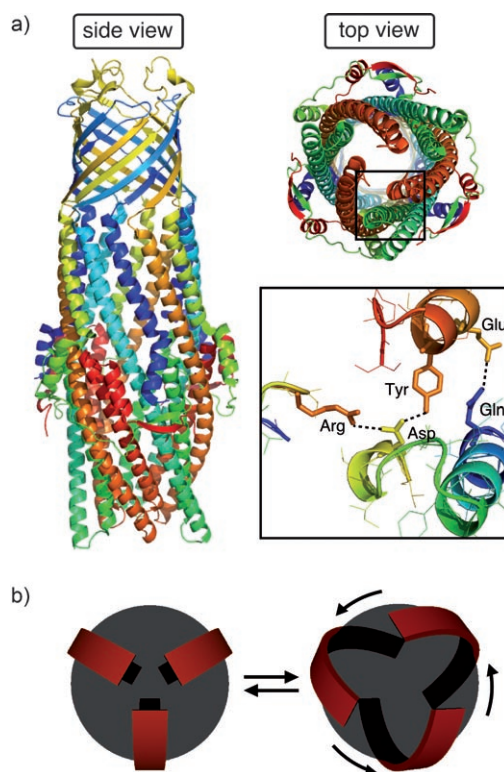

Figure 2. a) Structure of TolC (PDB code: 1TQQ) showing three-fold symmetry and a close-up view of intersubunit contact with protein side chains participating in hydrogen bonds and salt bridges denoted by dotted lines.[40b] b) Schematic representation of the iris-like opening and closing motions mediated by correlated twisting of three α-helical subunits of TolC.

entail severe steric clash between the bulky aromatics, thereby providing a self-correcting mechanism for this highly regulated conformational switching.

As shown in Figure 1 and Scheme 8, steric interactions play a critical role in simplifying the conformational space explored by the inherently flexible structure **19**, but they become a serious liability when the molecule approaches the flattened conformation. Upon structural folding, the *m*-terphenyl wing-tip groups in **20** (or **20′**) are brought within close van der Waals contacts and experience severe steric crowding. The situation is further exacerbated by the presence of three such pairwise interactions within the molecule. An attractive intersubunit interaction thus needs to be introduced to the wing-tip groups in order to avoid this undesired situation and facilitate structural folding toward a planar conjugated structure. As will be discussed in the following section, the inspiration for such molecular design came from naturally occurring constructs.

Dynamic 2D Conjugation: Inspirations from Biology

Fast and reversible conformational switching is a well-exercised mode of operation in many protein complexes participating in transport and signal transduction.[39] One such system, TolC, is an excellent example of molecular design to control such dynamic properties. This trimeric protein complex serves as an exit duct for materials transport through the cell membrane, and its opening and closing motions are mediated by a tight mechanical coupling of three α-helical subunits moving in concert.[40] As shown in Figure 2, each intersubunit contact of TolC is lined with a network of hydro-

gen bonds and salt bridges. The making and breaking of these multiple noncovalent bonds translate to large-scale tilting motions that effectively modify the pore dimension. Because of the molecular three-fold symmetry, local structural distortions occurring at one intersubunit contact of TolC should be transmitted to and reproduced at the two other symmetry-related sites. This ingenious amplification mechanism nicely showcases the functional relevance of symmetry in de-randomizing structural changes at both the molecular and supramolecular level.

A spring-loaded 2D-conjugated system **22 a,b** (Scheme 9) was subsequently designed to mimic the key functional features of the biological machinery discussed above.[41] Exploiting the established capacity of the O−H group to function as both hydrogen-bonding donor and acceptor, a cyclic array of an O−H···O−H network was constructed at the periphery of an inherently flexible 2D-conjugated structure represented by C_3-symmetric tris(*N*-salicylideneaniline).[38,42,43] The making and breaking of this noncovalent bonding network effectively interconverted the folded and unfolded conformers with maximum and minimum conjugation area, respectively (Schemes 6 and 9).
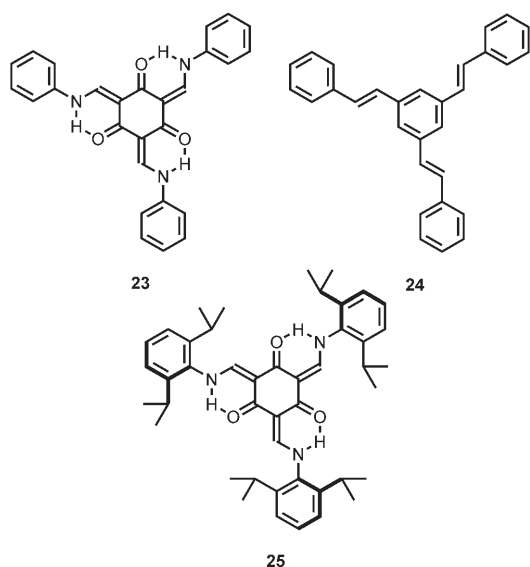
The C_3-symmetric tris(*N*-salicylideneamine) core of this molecular prototype 1) has one central ring surrounded by three hydrogen-bonded six-membered rings that trace the

larger π-conjugation area
stronger luminescence

smaller π-conjugation area
weaker luminescence

22a

22b
(R = tBu)
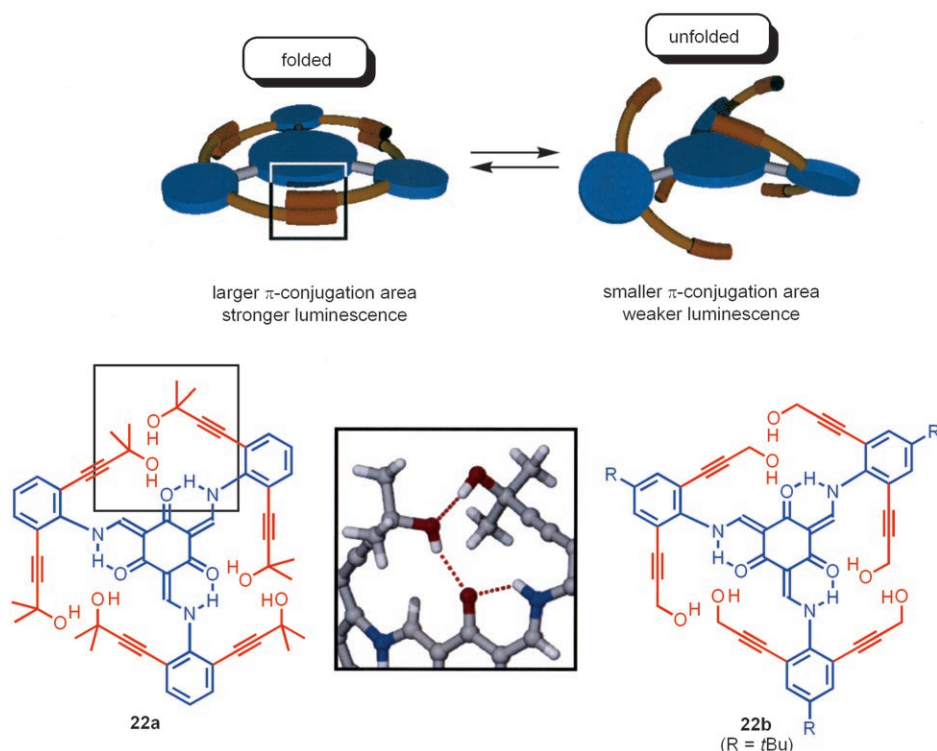
Scheme 9. Cooperative conformational switching: dynamic 2D conjugation is essentially spring-loaded with a C_3-symmetric hydrogen-bonding network, the disassembly of which leads to structural unfolding and loss of luminescence. Shown next to the chemical structure is a close-up view of this key secondary interaction determined by X-ray crystallography.[41, 45]

shape of trisubstituted triphenylenes, 2) brings three freely rotating aryl groups within a distance range that is ideal for correlated tilting motions, 3) provides a rigid platform for planar [n,π]/[π,π] conjugation, and 4) facilitates covalent assembly through highly convergent [3+1]-type Schiff base condensation from elaborate anilines and a trisaldehyde precursor.

As can be expected from a simple particle-in-a-box model (Scheme 6), an increase in the interplanar torsional angle τ

nicely correlated with the increase in the HOMO–LUMO gap of the DFT model compound **23** as well as its all-carbon analogue **24**.[44]

Dynamic 2D Conjugation: Emerging Structure-Property Relationships

Structural distortion fundamentally affects both the ground- and excited-state electronic properties of 2D conjugation. Hydrogen-bonded **22a** mimics the shape of the flattened and fully conjugated conformation of **13** shown in Scheme 6, and displays a significantly red-shifted UV/Vis absorption and emission spectra relative to **25** (Figure 3a).[41] The latter compound, due to the severe steric crowding induced by 2,6-diisopropyl substituents, adopts the geometry of the completely deconjugated structure shown in Scheme 6.[42] Apparently, structural folding and unfolding effectively expand and shrink the 2D conjugation area and directly impact the HOMO–LUMO gap.

The significantly smaller Stokes shift of **22a** compared with that of **25** (Figure 3b) indicates structural rigidification that should funnel excited-state energy to radiative decay channels. Consistent with this structure–property model, analogues of **22a** with essentially superimposable 2D conjugation pathways but lacking the crucial hydrogen-bonding net-
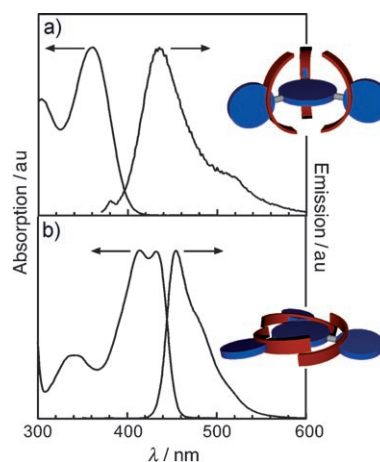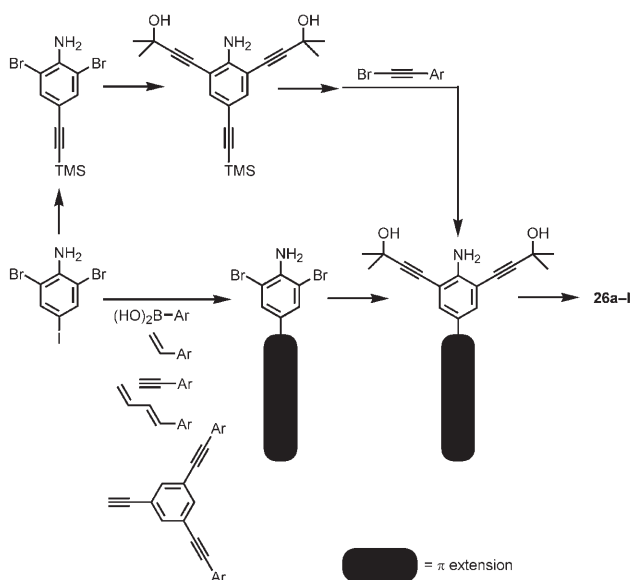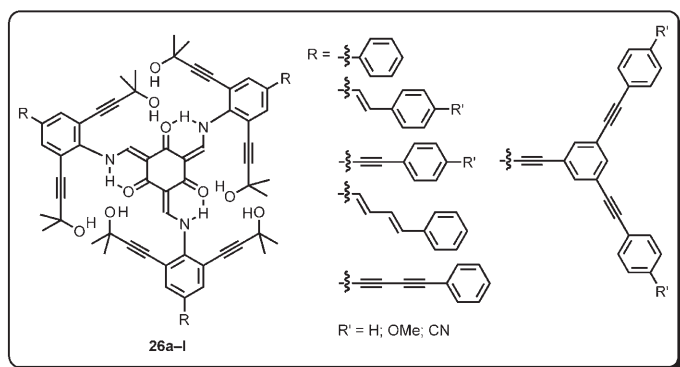

23   **24**

25

Figure 3. Normalized absorption and emission spectra of a) **25** and b) **22a**, and schematic representations of their solid-state structures.[41]

work display significantly diminished emission efficiency.[41] The reversible conformational switching of the 2D conjugation (Scheme 9) was eventually realized by addition and removal of F$^-$ to a solution sample of **22b**. The fluoride ions effectively disrupted the O−H···O−H hydrogen-bonding network, and quenched the fluorescence by facilitating nonradiative decay of the excited-states through internal torsional motions. Externally added TMSCl scavenged F$^-$ and thereby restored the blue emission of this compound.[41]

Structural Evolution: Ever Expanding 2D Conjugation

When one analyzes the reversible expansion and shrinkage of the 2D conjugation by using a simple particle-in-a-box model (Scheme 6), the smallest "box" corresponds to the tris(*N*-salicylideneamine) core. On the other hand, the dimensions of the largest box are essentially unlimited so long as the peripheral shell can be radially expanded without compromising electronic conjugation.

A highly modular synthetic scheme was developed (Scheme 10), by which twelve new compounds **26a–l**, with varying conjugation areas and electronic demands, were pre-

pared.[45] This synthetic exercise nicely showcased the efficacy of transition-metal-catalyzed C−C coupling in the stepwise construction of conjugated organic materials. The photophysical consequences of such structural modification strongly depend on the length of the radially elongated 1D subconjugation as well as on the nature of the spacers connecting phenylene units. A structural window could be defined, in which an increase in the conjugation area nicely correlated with systematic red shifts in electronic absorption/emission and increases in fluorescence quantum yields. Excessive branching of the peripheral groups, on the other hand, led to evolution of localized electronic structures and diminution of emission efficiency.[45]

A more drastic approach was taken with a multichromophore array **27** to control the photophysics of dynamic 2D conjugation by fluorescence resonance energy transfer (FRET) (Figure 4).[46] The molecular threefold symmetry of **27** places three BODIPY (BODIPY = boron dipyrromethene difluoride) fragments at the periphery of the tris(*N*-salicylideneaniline) core for an efficient FRET. Intriguingly, this dynamic array displayed a highly unusual signal amplifying behavior in which emission from the energy acceptor (= BODIPY) responded nonlinearly to the change in the energy donor (= tris(*N*-salicylideneaniline)) emission induced by binding and removal of F$^-$. This enhanced sensitivity allowed for the observation of sigmoidal binding isotherms in the fluorescence switching cycles (Figure 4). Such an allosteric behavior[47] provided convincing experimental

26a–l

R =

R' = H; OMe; CN

Scheme 10. Modular synthesis of extended 2D conjugation.[45]
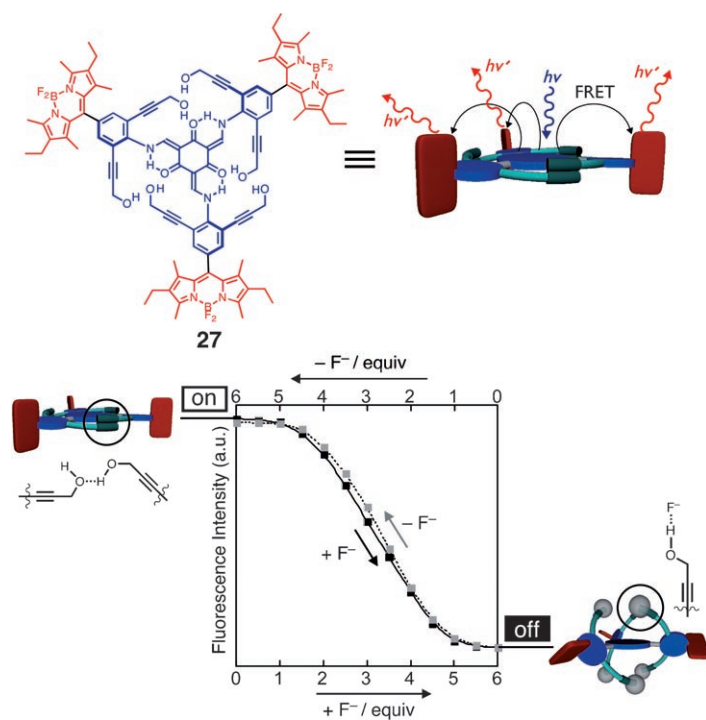
= π extension

27

Figure 4. A dynamic FRET system **27**, comprising a central energy donor (in blue) and peripheral energy acceptor (in red) units, responds reversibly to the addition and removal of F$^-$.[46] The sigmoidal isotherms observed in the turn-on and turn-off switching scans are diagnostic of cooperativity in multisite binding events.

evidences for the cooperativity in structural folding and unfolding proposed in Scheme 9.

Summary and Outlook

Increasing the spatial dimensionality of electronic conjugation increases structural complexity and allows for integration of additional functionalities for both intra- and intermolecular secondary interactions. Electronic conjugation in 2D settings offers opportunities 1) to spatially separate molecular orbitals that fundamentally affect the ground- and excited-state electronic properties, 2) to control mixing of localized and delocalized components of the electronic structures associated with cross-linking, 3) to establish well-defined spatial relationships between segments of 1D donor and acceptor units in electron/energy transfer, and 4) to guide assembly of higher-order structures functioning as well-defined conduits for charge and/or energy carriers.

Additionally, cooperative noncovalent interactions within inherently dynamic 2D conjugation allow for dynamical control over both the ground- and excited-state electronic properties of structural domains beyond molecular wires. New research avenues branching out of this emerging class of controllable 2D conjugation are expected to complement and challenge existing paradigms in electronically conjugated molecules and materials.

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