How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 24543–24548
International Edition: doi.org/10.1002/anie.202107893
German Edition: doi.org/10.1002/ange.202107893

VIP *π-Conjugated Macrocycles* *Very Important Paper*

Naphthodithiophene Diimide Based Chiral π-Conjugated Nanopillar Molecules

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Abstract: *The synthesis, structures, and properties of [4]cyclonaphthodithiophene diimides ([4]C-NDTIs) are described. NDTIs as important n-type building blocks were catenated in the α-positions of thiophene rings via an unusual electrochemical-oxidation-promoted macrocyclization route. The thiophene–thiophene junction in [4]C-NDTIs results in an ideal pillar shape. This interesting topology, along with appealing electronic and optical properties inherited from the NDTI units, endows the [4]C-NDTIs with both near-infrared (NIR) light absorptions, strong excitonic coupling, and tight encapsulation of* C_{60}. *Stable orientations of the NDTI units in the nanopillars lead to stable inherent chirality, which enables detailed circular dichroism studies on the impact of isomeric structures on π-conjugation. Remarkably, the [4]C-NDTIs maintain the strong π–π stacking abilities of NDTI units and thus adopt two-dimensional (2D) lattice arrays at the molecular level. These nanopillar molecules have great potential to mimic natural photosynthetic systems for the development of multifunctional organic materials.*

Introduction

The breadth of structure and function displayed by molecules found in nature is remarkable. In bacterial photosynthesis, highly symmetric cyclic arrangements of chlorophyll units support highly delocalized excited states enabling efficient energy transfer between the constituent chromophores. Furthermore, the cyclic architecture is effective in constructing densely packed two-dimensional (2D) arrays to ensure efficient photon capture, and to facilitate the rapid, efficient, and directional energy flow between adjacent antennas.[1] With cyclic arrays being a natural choice, synthetic π-conjugated macrocycles, particularly with strained π-systems, have identical sites in the symmetric ring, leading to more delocalized excited states.[2] Accordingly, creation of novel strained π-conjugated macrocycles with organized 2D lattice superstructures through self-assembly have the potential not only to circumvent the problems in state-of-the-art artificial photosynthesis but also to influence the development of luminescent materials, photocatalysts, solar cells, optical sensors, etc.[3]

Recent studies have shown that tessellation of tubular cyclophanes[4] and pillararenes[5] led to formation of 2D square and honeycomb tiling patterns. In this context, carbon nanohoops with conjugated structures, like [*n*]cycloparaphenylenes (CPPs)[6] and π-extended (naphthalene,[7] anthracene,[8] chrysene,[9] anthanthrene,[10] hexa-peri-hexabenzocoronene,[11] fluorene,[12] benzothiadiazole,[13] thiophene[14]) CPP analogues appeared to be suitable frameworks in an attempt to mimic the light harvesting complexes. However, these distorted structures all have considerably high torsional angles (θ: ca. 27–35°) caused by C–H/C–H steric interactions, resulting in less π overlaps and evident decrease in conjugation between the neighboring aromatic rings,[15,16] further hampering the face-to-face arene–arene stacking, as is often observed for linear arene systems[17] (Scheme 1 a). This encourage us to pursue novel CPP analogues which possess broad absorption region matching the solar spectrum, high degree of exciton delocalization,[18] and especially the highly ordered 2D molecular packing.

Compared to the phenyl–phenyl subunit that distinctly deviates from planarity, a five-membered thienyl–thienyl subunit can obtain a much smaller torsional angle that allows for desirable intrachain orbital delocalization.[19] As such, the

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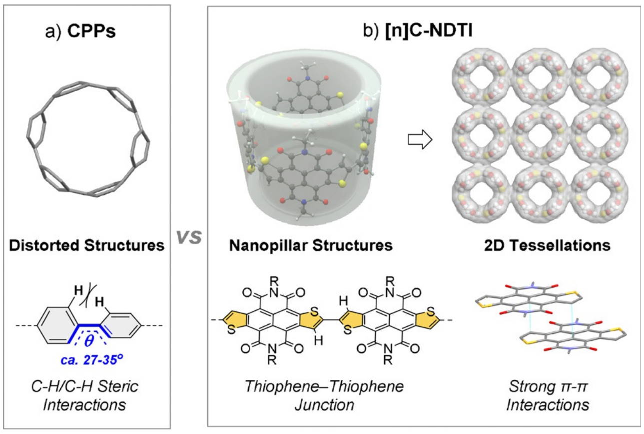
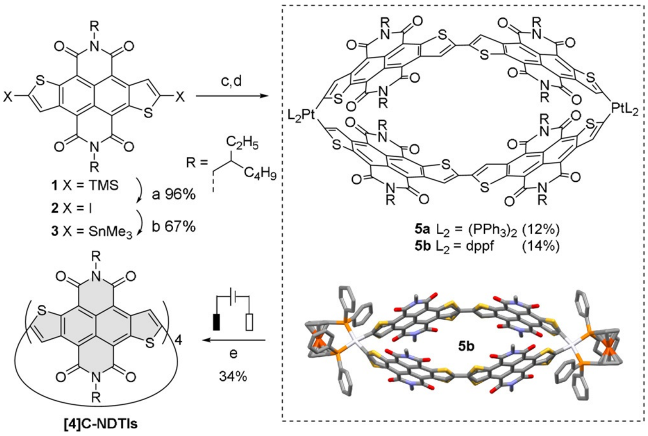


Scheme 1. From a) CPPs to b) nanopillar molecules [*n*]C-NDTIs ([6]CPP from ref. [12a]).



Scheme 2. Synthetic procedures toward [4]C-NDTIs. a) ICl, 96%; b) Sn_2Me_6, $Pd(PPh_3)_4$, 67%; c) $Pt(COD)Cl_2$, 97%; d) phosphine ligand; with PPh_3: 12%; with dppf: 14%; e) electrochemical oxidation, 34% (for **5b**, 1.4 V); 13% (for **5a**, 1.6 V). For clarity, ethylhexyl groups and H atoms of crystal structure **5b** are omitted, the S atom was found to be disordered with the C atom in the thiophene ring.

C_{2h}-symmetric naphthodithiophene diimide (NDTI),[20] with naphthalenediimide (NDI) core terminated in two thiophene rings, represents an ideal building block for nanopillar molecules referred to as cyclic-NDTIs (C-NDTIs). NDTI offers the advantages that: 1) it has interesting electronic and optical properties and is utilized as active materials in organic electronics devices;[21] 2) effective accumulation of NDTI cores through the thiophene–thiophene junction allows strong conjugation; 3) electron deficient nature as well as intermolecular donor (thiophene)–acceptor (NDI) interactions of the large rigid planar NDTI framework favor strong intermolecular π–π overlaps (Scheme 1b).[20]

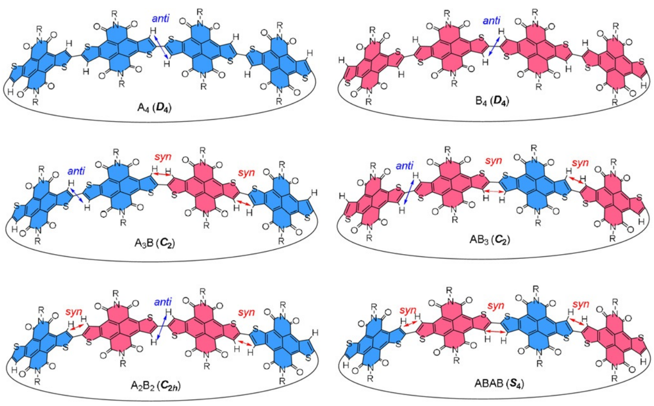
However, the NDTI units have redox-active natures as well as electron-deficient properties, which make them challenging building blocks for construction of the strained π-conjugated macrocycles. By now, oxidative or reductive aromatization of C(sp^3)-containing macrocycle precursors and reductive elimination of Pt molecular squares are two common synthetic routes toward CPPs and their analogues.[22] The Pt-mediated macrocyclization method seems to be the only choice for construction of C-NDTIs, but is confronted with difficulties in reductive elimination due to strong bonds between Pt and electron-withdrawing NDTI ligand[23] as well as high ring strains.[24] Other than that, the redox-active natures of NDTI units further narrow the choice of redox reagents that can promote the macrocyclization. Herein, we report the first synthesis of [4]C-NDTIs via an electrochemical-oxidation-promoted macrocyclization route, which adopt ideal pillar shapes and have outstanding optical properties along with the ability to bind together in 2D lattice arrays at the molecular level.

Results and Discussion

Synthesis and Isolation. Scheme 2 depicts our synthesis of [4]C-NDTIs. The key building block 2,6-bis(trimethylsilyl)-NDTI (**1**) was readily synthesized by oxidative cyclization of 2,6-bis(trimethylsilyl)ethynyl-NDI with K_2S.[20,25] NDTI unit **1** was then converted into 2,6-bis(trimethyltin)-NDTI (**3**) via successive iodination and stannylation in high yields. Transmetalation of $[Pt(COD)Cl_2]$ with **3** was performed at 45 °C in THF for 2 days. Because pure tetranuclear Pt-complex **4** is not stable during the isolation, the resulting complex mixture was directly subjected to the ligand exchange and reductive elimination reactions. Treatment of **4** with excess triphenylphosphine (PPh_3)[9a] or 1,1′-bis(diphenylphosphino)ferrocene (dppf) only afforded the corresponding binuclear platinum complex **5a** or **5b**. Their structures were established by single-crystal X-ray diffraction analysis (Figure S1, CCDC 2087509, 2098014). Thermally activated reductive eliminations from **5** were impeded because of the strong bonds between Pt and NDTI ligand and high ring strain energy of [4]C-NDTIs.[23,24] Moreover, oxidant-induced reductive elimination of **5b** in the presence of AgOTf, Br_2, XeF_2, and $NOBF_4$ were also proved unsuccessful due to incompatibility of the NDTI units with these chemical oxidants (Table S1).

We then evaluated the redox properties of **5** using cyclic voltammetry (CV). For **5a** and **5b**, first irreversible oxidation waves were observed at $E_{p1} = 1.4$ V and 1.1 V (vs. Ag/AgCl, Figure S2), respectively. It is anticipated that, within the time scale of the electrochemical measurement, the complexes underwent fast reductive elimination, rendering the oxidation irreversible. Thus, the electrochemical-activated reductive elimination of **5b** was performed with a constant cell potential. After several attempts, the desired [4]C-NDTIs were isolated as a purple solid with 34% yield at $E = 1.4$ V. Similar transformations of **5a** should be conducted at a higher potential (1.6 V). However, the yield (13%) of [4]C-NDTIs was lower perhaps due to an overoxidation.[26]

As a rigid π-conjugated macrocycle, [4]C-NDTIs display a good solubility in common organic solvents, such as dichloromethane, chloroform, tetrahydrofuran and toluene. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry of the product gives a mass/charge ratio (m/z) value of 2402.737 (Figure S3), which matched well with the value calculated based on the chemical composition of the molecule ($C_{136}H_{144}N_8O_{16}S_8$ $[M]^-$: 2402.851).



Scheme 3. Six possible isomers of [4]C-NDTIs; the orientation of the NDTI units marked as A and B denoted with blue and red, respectively.

Depending on the relative orientations of the NDTI units in the macrocycle, the macrocyclization product should contain six stereoisomers including two sets of enantiomers and two other diastereomers (Scheme 3).[27] However, our sample displayed only one single spot on the TLC plate. Using chiral high-performance liquid chromatography (HPLC), we isolated five sets of the six isomers (Figure S4: **I** 33.8 %, **II** 9.0 %, **IV** 14.0 %, **V** 9.2 %, **VI** 30.4 %. **III** was observed in analytical HPLC, but the insufficient amount obtained constrained its further characterization).

Circular Dichroism (CD) and Theoretical Calculations. An unambiguous assignment of enantiomers could be provided by a study of the CD responses of the isomers. We determined experimental CD spectra of the cyclic systems dissolved in toluene at 25 °C.[28] As shown in Figure 1 a, the CD spectrum of **I** and **II** are the mirror images of the spectra for **VI** and **V** respectively, which indicates that **I**/**VI** and **II**/**V** are pairs of enantiomers.[29] **IV** is totally CD-silent. Then, computational studies of the molecular structures were performed at the level of density functional theory (DFT) in conjunction with the B3LYP functional,[30] 6–31+G(d) basis set,[31] and D3 corrections[32] to account for dispersion interactions. We considered all six isomers A_4, B_4, A_3B, AB_3, A_2B_2, and ABAB and found their optimized structures to span the molecular point groups of D_4, C_2, C_{2h}, and S_4, respectively. The enantiomeric isomers A_4/B_4 are the most stable ones with optimized Gibbs energies that are lower compared to others by some 3.2 (A_3B/AB_3), 3.3 (A_2B_2), and 7.0 kcal mol^{-1} (ABAB) (Figure S5). CD spectra for the optimized structures of A_4/B_4 and A_3B/AB_3 were calculated (Figure 1 b). The theoretical CD spectra of these enantiomers are in good agreement with the experimental results. We therefore assign isomer **I** as A_4, isomer **II** as A_3B, isomer **V** as AB_3 and isomer **VI** as B_4.

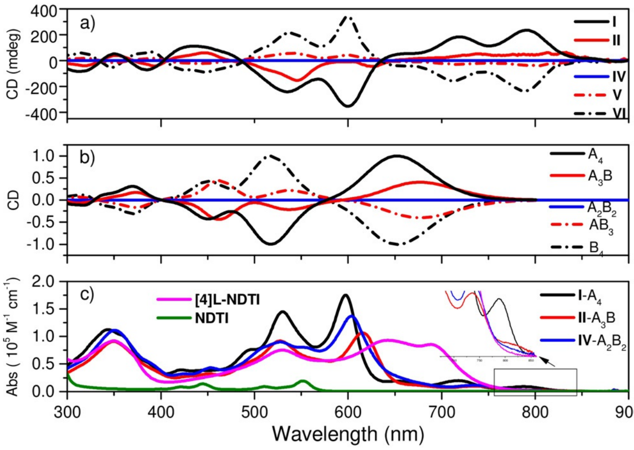


Figure 1. a) Experimental and b) theoretical CD spectra of [4]C-NDTI isomers; c) UV/Vis-NIR spectra of [4]C-NDTI isomers, [4]L-NDTI, NDTI (10 μM in toluene).

NMR Analysis. Considering the symmetric structures of the isomers shown in Scheme 3, the numbers of inequivalent protons at β-position of thiophene rings in A_4/B_4, A_3B/AB_3, A_2B_2, and ABAB should be 1, 4, 2, and 1, respectively. Figure 2 displayed the NMR spectra of three isomers (**I**, **II**, and **IV**). One singlet peak of isomers **I**-A_4 at 8.92 ppm further proved its D_4 symmetry (Figure 2 c). Four signals of isomer **II**-A_3B are consisted with its C_2 symmetry (Figure 2 b). At last, two signals for isomer **IV** allowed us to assign it as A_2B_2 with C_{2h} symmetry (Figure 2 a). The upfield shifts of the protons in [4]C-NDTIs isomers compared with the NDTI monomer **1** reflected an influence of the ring current of adjacent NDTI units (Figure 2 d).[33] For isomers **II**-A_3B and **IV**-A_2B_2, the thiophene protons in *syn*-conformation exhibit low-field shifts due to nonbonded repulsions between compressed hydrogens.[34]

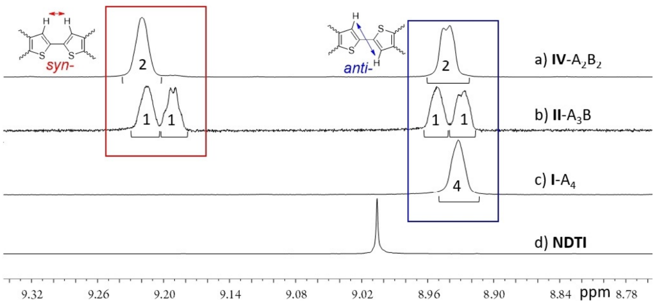


Figure 2. ^1H NMR spectra (850 MHz, 1 mM in $CDCl_3$) of a) **IV**-A_2B_2, b) **II**-A_3B, c) **I**-A_4, d) NDTI in the aromatic region at room temperature.

X-ray Crystal Structures. Single crystals of isomers **I**-A_4 and **IV**-A_2B_2 suitable for X-ray diffraction analysis were obtained by diffusing methanol slowly into their 1,1,2,2-tetrachloroethane solutions. The crystals of **I**-A_4 (CCDC 2087156) and **IV**-A_2B_2 (CCDC 2087154) are in *C*2 and *C*2/*m* space groups, respectively. As expected, both of the two [4]C-NDTIs isomers adopted cylindrical conformations (Figure 3 and Figure 6). The average diameter of the cavity is ca. 1.4 nm. For **I**-A_4, the torsional angles between the NDTI monomers are only 4.4° and 2.8°, much lower than that of [*n*]CPPs (ca. 27–35°). All possible torsional angles for **IV**-A_2B_2 are not more than 9.3°.[35] The calculated torsional angles range from 3.8° to 9.4° for all the six isomers, which agrees well with the experimental X-ray crystallographic data (Figure S7).

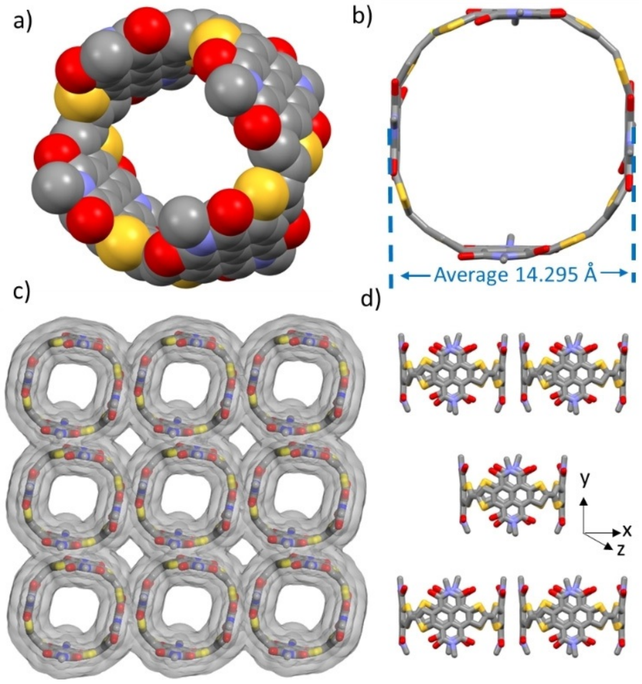


Figure 3. a, b) Crystal structure of **I**-A_4. Superstructure of [4]C-NDTIs: c) 2D tetragonal tiling of the [4]C-NDTIs through π–π interactions; the transparent van der Waals surface of the [4]C-NDTIs is shown to illustrate the effective pillar cavities and intermolecular interactions; d) Staggered arrangement along the *y* axis; for clarity, ethylhexyl groups, all H atoms, and solvent molecules are omitted.

More importantly, the NDTI unit in [4]C-NDTIs can further stack in a "parallel offset" manner with another NDTI unit in one adjacent macrocycle through close π-interactions. As a result, the pillar shape **I**-A_4 and **IV**-A_2B_2 both self-assemble in a tetragonal manner to form a 2D layer-like square tessellated pattern (Figure 3c). Along the *y* axis, the macrocycles stack with a staggered pattern, forming a non-tubular superstructure (Figure 3d). The unique 2D topology of the superstructures combined with the end-free strong π-conjugation of the monomers should facilitate both intra- and intermolecular contacts and charge transport.

Photophysical Properties and Encapsulation of Fullerene (C_{60}). The interesting topology, along with rich properties inherited from the NDTI units, endows the [4]C-NDTIs with unique physical properties. The photophysical properties of three [4]C-NDTIs isomers (**I**-A_4, **II**-A_3B, and **IV**-A_2B_2) and linear tetramer [4]L-NDTI for sake of reference were compared (Figure 1c). The absorption spectrum calculations were also performed (Figure S8). The main features of the experimental spectra are well captured.

Compared to CPP analogues and other strained macrocycles involving porphyrin[33,36] and perylene diimide (PDI) units,[37] employing NDTI as building blocks for the nanopillar molecules brings about near-infrared (NIR) spectra up to ~850 nm due to more effective conjugation of ring segments (Figure 1c). In contrast to the full range of NDTI–NDTI torsional angles populated in [4]L-NDTI, much sharper and more structured absorption spectra of [4]C-NDTIs reflect their well-defined rigid conformations, and evident red shifts in the spectra indicate small NDTI–NDTI torsional angles in these systems.[2] All of these nanopillars have lower fluorescence quantum yield (≈0.04%) than the linear oligomer (≈0.2%, Figure S9a) and NDTI (88%, Figure S9b). Low absorption strengths of the cyclic complexes at long wavelength as well as the low fluorescence quantum yields could be explained in terms of a symmetry-forbidden transition, confirming that their excited state are delocalized over the whole π-systems.[2a]

In addition, the stable *anti-* and *syn*-conformations of thiophene rings in adjacent NDTI units have significant influence on the overall conjugation and can consequently reveal how strain and curvature influence π-conjugation. In the near-UV region, an analogous absorption band is found for all [4]C-NDTIs isomers. The main absorption bands are found in the region from 500 to 650 nm with a distinct splitting into two bands for isomer **I**-A_4 and similar but less distinct splitting for **II**-A_3B and **IV**-A_2B_2. The characteristic band splitting is seen also in the CD spectra of **I**-A_4 and **II**-A_3B, both peaks for both isomers showing negative Cotton effects. The intensity ratio of the two peaks differs significantly between the two isomers, which is also well reproduced in the theoretical spectra (Figure 1). For **I**-A_4, the lower-energy peak dominates in intensity whereas the opposite holds true for **II**-A_3B. In the region between 650 to 800 nm, **I**-A_4 shows significant absorption. Interestingly, there are multiple strong positive CD peaks in this region and which are likely correspond to vibrational progressions of a single electronic transition. Combined, the dichroisms in the NIR and visible regions demonstrate the bisignate CD signal response that is characteristic for systems with strong excitonic coupling.

The rigid pillar shape with large NDTI plane enables the [4]C-NDTIs to be an ideal system to hold a fullerene, which could mimic cyclic arrangement of chromophores with a functional reaction centre in light-harvesting apparatus.[3] The binding constant of **I**-$A_4 \supset C_{60}$ in toluene was measured to be $(1.86\pm 0.08)\times 10^8\ M^{-1}$ by fluorescence titration (Figure S11). This high binding constant shows that the cavity size and the NDTI units both play a crucial role in binding with C_{60}.

Conclusion

In summary, from a supramolecular perspective, we designed and synthesized [4]C-NDTIs via the electrochemical-activated reductive elimination of cyclic bisplatinum complexes. To the best of our knowledge, this is the first example of synthesizing π-conjugated macrocycles using an electrochemical route. The incorporation of rigid NDTI units not only imbues the macrocycles with an ideal pillar shape along with a wealth of unique optical and chiral properties, but also render them ideal building blocks for constructing a 2D supramolecular architectures. These features provide valuable opportunities to mimic natural photosynthetic systems. On a more practical level, like fullerene derivatives with high rigid spherical structures that enhance π electrons delocalization and multidimensional charge transporting capabilities, nanopillar molecules represented by [4]C-NDTIs can play significant roles in the development of organic electronic and optoelectronic materials. This work may open the way to a broader use of electrochemical reduction in the synthesis of cyclic conjugated molecules. More importantly, the 2D stacking ability of these novel π-conjugated nanopillar molecules will stimulate the study on multidimensional assembly in supramolecular chemistry.

Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China (No. 22071208, 21772165, 21772162), the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (Grant No. 21521004), Youth Innovation foundation of Xiamen (3502Z20206058), the Fund for Scientific Research (F.R.S.-FNRS, Grants Nos. 4532.16 and 30650939), the Swedish e-Science Research Center (SeRC), the Swedish Research Council (Grant No. 2018–4343), and the European Commission (Grant No. 765739) as well as computer resources from the Swedish National Infrastructure for Computing (SNIC).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: conjugation · cycloparaphenylenes · macrocycles · nanopillar molecules · naphthodithiophene diimide

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[27] Although the 2-ethylhexyl substituents on nitrogen atoms have a chiral center, they were introduced in racemic forms. Furthermore, the chirality in side chains always provides only weak perturbations to the electronic transitions of main chromophores. No actual effects of 2-ethylhexyl substituents on the chiral characteristics of [4]C-NDTIs were observed.

[28] Temperature/Solvent-dependent CD measurements of [4]C-NDTIs indicate that all isomers are molecularly dissolved monomers in toluene at 25 °C.

[29] With HPLC separation, **V**-AB$_3$ and **VI**-B$_4$ show overlapping peaks, thus tiny **VI**-B$_4$ may still exist in the sample of **V**-AB$_3$, leading to imperfect mirror CD shape.
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Manuscript received: June 14, 2021
Accepted manuscript online: July 21, 2021
Version of record online: August 18, 2021