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Fullerene-Filled LC Stars – A Supramolecular “Click” Mechanism for the Generation of Tailored Donor- Acceptor Self-Assemblies

Matthias Lehmann, Moritz Dechant, Marco Holzapfel, Alexander Schmiedel, Christoph Lambert*

ABSTRACT: *Two shape-persistent star mesogens with oligo(phenyleneethenylene) arms and a phthalocyanine core – one providing free space (**2**) and one sterically overcrowded with four fullerenes attached by spacers (**3**) – have been successfully synthesized. In contrast to a smaller discotic derivative **1**, mesogen **2** forms a columnar liquid crystal (LC), which can only be partially aligned without π-stacking, while **3** is not an LC. Exceptionally, the 1:1 mixture of **2** and **3** forms an alignable columnar LC with strong π-stacking and quadruple helical organized fullerenes by an unprecedented click process similar to a ball detent mechanism. The C_{60} units interconnect also different columns. This is driven by nanosegregation and space-filling of the voids with fullerenes. Photophysical studies confirm the presence of a light collecting system generating charge separated states in solution and solid state, which makes such highly organized materials attractive for the study in future photovoltaic devices.*

The coupling of building blocks of different nature in a final synthetic step is an attractive task for the development of advanced materials. In the last two decades the click concept, introduced by B. Sharpless, was successfully applied for this purpose, however, thereby the compounds are joint irreversibly by covalent bonds.[1] Click chemistry with dynamic covalent bonds and even supramolecular click chemistry were later presented, which widen the scope to temporary connections.[2-4] However, these concepts do still not model macroscopic inventions that can be opened and closed reversibly, namely velcro fastener, snap fit buckels, snap fasters and ball detents. These mechanisms rely exclusively on the shape of the two different components – the “host” providing space for the “guest” counterpart linking these units mechanically. Here, we present a supramolecular “Click” procedure reminiscent of the ball detent mechanism fixing the position of star-shaped zinc phthalocyanins (ZnPc) **2** and **3** (Figure 1) with regular π-π distances to the center of liquid-crystalline (LC) columns. The mesogens **2** with long oligo(phenyleneethenylene) arms do not naturally assemble by π-π stacks and compensate the intrinsic free space by dimer propeller formation.[5] In the mixture, C_{60} fills the free space between the conjugated arms, producing a filled LC phase with a ZnPc donor stack surrounded by a fullerene acceptor quadruple helix. Filled mesophases were first reported by Pelzl and Weißflog and space-filling has been shown also to be important in the CPI concept or the LC shuttlecocks.[6-8] Recently even an empty macrocycle has been reported to form a LC pseudorotaxane with a linear dicyano derivative.[9] The dyad combination of fullerenes and phthalocyanines or porphyrines have been previously intensely studied as promising materials for future organic photovoltaic devices owing to their charge formation and transport properties.[10,11] These shape-amphiphiles segregate because of their large differences in morphology between the spherical C_{60} and the large flat phthalocyanines and helical arrangements of the fullerenes were frequently suggested. The helical stacking in triple helices has been recently substantiated in star-shaped oligo(phenylenevinylene) mesogens bearing fullerene bound by a short spacer by means of WAXS and SAXS, modeling with materials studio and fiber diffraction simulation.[12] The present parent star-shaped target molecules **1** and **2** (Figure 1) consists of a larger zinc phthalocyanine (ZnPc) core decorated with oligo(phenylenevinylene) arms. The derivative with extended arms **3** is equipped with four fullerenes, attached via long spacers to the conjugated arm scaffold. The periphery has been chosen to be oligo(ethyleneoxy) chains, since they are known to lower the transition temperatures and in case of future applications they would lead to higher relative permittivities facilitating the charge separation.[13] We highlight that extending the arm length from n = 0 in **1** to n = 1 in **2** the thermotropic properties and packing changes dramatically owing to the need of space filling. While in material **2** π-stacking is almost absent, it is recovered when mixed with non-mesomorphic compound **3**, which is a consequence of the click process. The result is a unique donor-acceptor nanostructure. Photophysical studies were performed to confirm energy transfer processes and the formation of charge separated states.

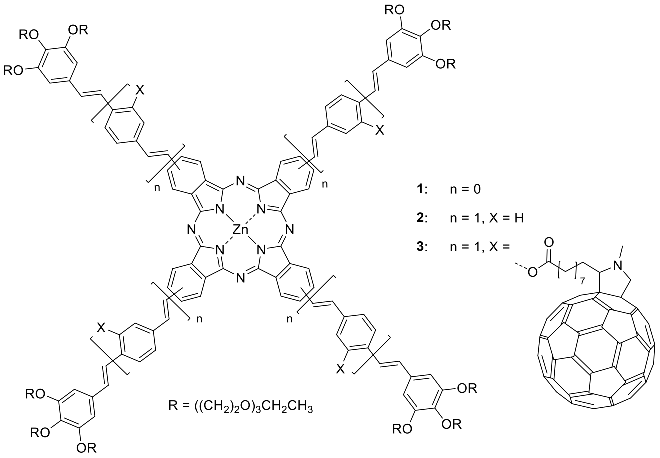

Figure 1. Target star mesogens.

The synthesis of the new ZnPc compounds **1-3** was performed by a convergent strategy with a final fourfold condensation of dicyanobenzene derivatives **6a-b** and **11** (Scheme 1). The stilbenoid arms were assembled by Wittig-Horner reactions and functional group interconversions using the intermediates **4**,**5**,**7**,**8** (Scheme 1 and Supporting Information), which were synthesized analogous to the known derivatives with aliphatic chains.[12,14] Compounds **6a-b** were condensed to obtain the ZnPc derivatives **1** and **2** in moderate yield between 22-27 %. The fourfold condensation of compound **11**, the deprotection and fourfold esterification yielded the fullerene derivative **3** in 6 % yield. All materials were analyzed comprehensively by standard analytical techniques (NMR, mass spectrometry and elemental analysis see supporting information). The target molecules were obtained as a mixture of four regioisomers, namely (2,9,16,24)-, (2,9,17,24)-, (2,10,16,24)- and (2,9,16,23)-

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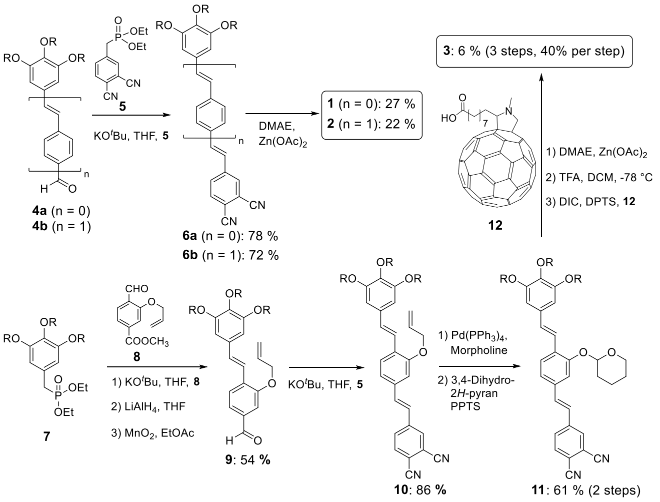
tetrasubstituted derivatives. In theory, they are statistically formed in the ratio of 4 : 2 : 1 : 1.[10a] The regioisomers could not be analyzed in detail by NMR spectroscopy because of broad, overlapping signals for the ZnPc protons (see Figures S1-4). Especially, the strongly aggregating compound **3** furnished only moderately resolved ^{1}H NMR spectra even at temperatures above 90 °C in $C_2D_2Cl_4$ (see Figures S3,4). Interestingly, compounds **1** and **2** revealed a completely different solubility. While **1** is soluble in aqueous solution and all common organic solvents except completely nonpolar liquids such as hexane, compound **2** is insoluble in hexane and aqueous solutions. The latter points to the increased hydrophobicity of the core and the larger hydrophobic pockets.



Scheme 1. Synthesis of the target compounds **1**-**3** (R = $(C_2H_4O)_3C_2H_5$); DCM dichloromethane, DIC diisopropylcarbodiimide, DMAE dimethylaminoethanol, DPTS dimethylaminopyridinium toluenesulfonate, PPTS pyridinium toluenesulfonate, THF tetrahydrofuran, TFA trifluoro acetic acid.

The thermotropic properties have been studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray scattering (XRS) on aligned fibers. POM photographs of compounds **1** and **2** at 220 °C of the sheared samples demonstrate their birefringent and fluid nature and thus confirm the LC properties (Figures 2A, S7). Unexpectedly, the star mesogens did not clear into an isotropic phase but decomposed at temperatures above 300 °C, which prevented the formation of characteristic LC textures. Compound **3** is found to be an amorphous solid. DSC confirm for all materials the absence of phase transitions from ambient temperature to 300 °C (Figure S8). Detailed structural information have been obtained for **1** and **2** from temperature-dependent wide-angle XRS (WAXS) (Figure 2). The first tremendous difference between compounds **1** and **2** is observed in the alignment of the two fibers. While the XRS pattern of **1** shows typical features of an oriented columnar phase of discotic molecules the pattern of **2** exhibits only weak or almost no alignment (Figures 2D,E). The small angle reflections for both compounds can be indexed according to a hexagonal 2D positional order. The cell parameters increase as expected from 38.1 Å (**1**) to 50.1 Å (**2**) at room temperature for the shape-persistent molecules, which is in good agreement with the molecular size (Figure S14). The halo at 4.5 Å and the signal corresponding to 3.4 Å can be attributed to the average distance of hydrocarbons including the liquid order of aliphatic chains and the π-π distance of the ZnPc cores. While for the essential discotic mesogens **1** a clear reflection for π-π distance of the ZnPc cores is discerned, for the larger derivative **2** this signal is almost absent indicating the low order of the ZnPc cores along the columns. In order to clarify the structural differences, the density has been measured by the buoyancy method for extruded fibers at room temperature (see SI). While for **1** the density could be only estimated in non-polar solvents to be in the range of 1.04 to 1.29 gcm^{-3} owing to solubility reasons, the value for **2** were determined to be 1.18 gcm^{-3} using aqueous $CaCl_2$ solutions. Combining XRS and density data the number of molecules **1** in a unit cell (a = 38.0 Å, c = 3.3 Å) can be estimated to be one at a density of 1.20 gcm^{-3}, whereas there are two molecules **2** in the columnar stratum (a = 50.1 Å, h = 4.6 Å, δ = 1.18 gcm^{-3}). Compound **1** forms a rather conventional columnar stack of discotic molecules, which is visualized in Figure 2I for the geometry optimized columnar stratum of six mesogens, modeled using Materials Studio using the major regioisomer.

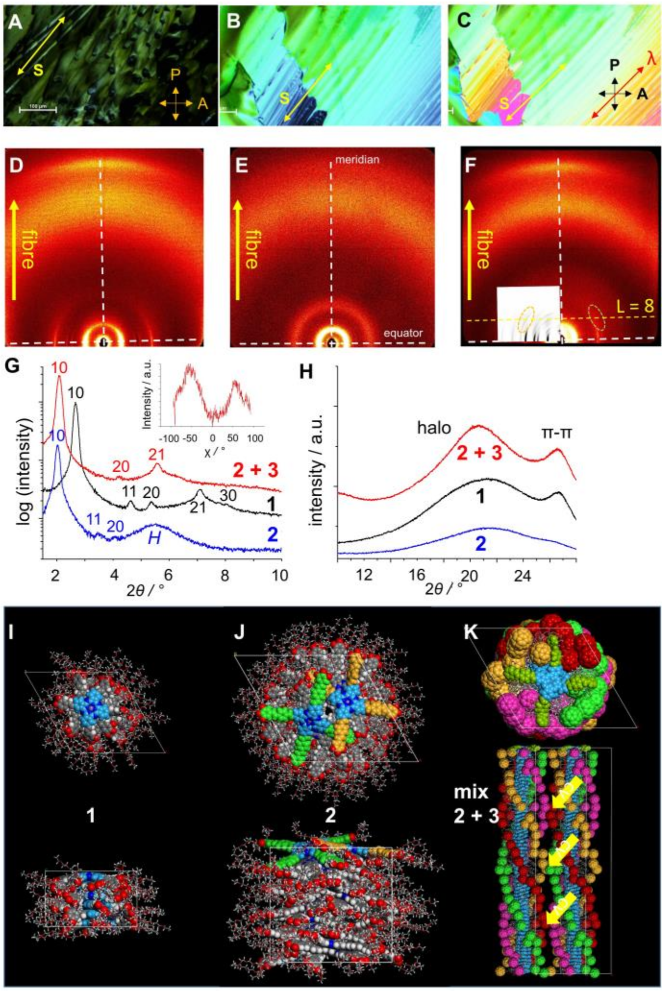


Figure 2. POM textures of shear aligned compounds **2** (A) and mixture **2**+**3** (B,C) (S shearing direction, P Polarizer, A Analyzer, λ direction of compensator plate). The mixture **2**+**3** reveals much better alignment (B) and the λ-compensator confirms an optical negative columnar phase (C). WAXS pattern of the hexagonal phases of **1**, **2** and the 1 : 1 mixture of **2 + 3** at 25 °C (D - F). Inset in F: Fiber diffraction simulation based on the model (K). G: Integrated intensity along the equator of the patterns with indexation confirming the Col$_h$ structure. The broad intensity H is attributed to the helical packing of **2**. Inset: χ-scan of the pattern of **2**+**3** between 2θ = 5-6° revealing the splitted intensities along the meridian. H: Integrated intensity along the meridian demonstrating the LC nature of the phases, with the broad halo and the intense signal for the π-π distance in case of compound **1** and the mixture **2+3**. I-K: models of the columnar phases of **1**, **2** and the mixture **2**+**3**. The ZnPc cores are colored in light blue, the stilbenoide arms are highlighted in orange and green. For the model of the mixture, the chains have been omitted for clarity; the yellow arrows show the interaction points of fullerenes from different columns.

In order to pack two molecules **2** in its columnar stratum the molecules can be neither side by side nor on top of each other for steric reasons. The most convenient packing is achieved by the propeller-like intercalation of two mesogens, thus filling almost three of the four intrinsic free spaces between the conjugated arms, similar to the model of Maier et al..[5] In order to avoid steric congestions along the column, the neighboring dimer has to be turned by at least 40° about the columnar axis, which is reminiscent of the stacking of octahedral metallomesogens (Figure S15).[15] The subsequent assembly affords a complete double helix with a pitch of 41.1 Å after nine dimers. The broad intensity *H* at 16.0 Å (2θ = 5.5°) in Figure 2E,G indicates indeed the presence of a periodicity along the column axis, which might be explained by such a helix. Owing to the missing alignment, we lack information about the position of this intensity along the meridian and thus about the details of the intra columnar structure. Nevertheless, the described double helical stack of **2** has been geometry optimized until large non-covalent energies were obtained (Figure 2J), substantiating the stability of this model assembly. The correlation length corresponding to the *H* signal is calculated with the full-width at half maximum according the Scherrer formula and amounts to approx. 80 Å, which is two helical pitches of our model structure.[16,17] The low shape anisotropy of this columnar assembly (diameter 50 Å, length 80 Å) provides a natural reason why the material cannot be easily oriented by extrusion. Thus the model confirms the nanosegregation and the efficient space-filling of the intrinsic void leading to the absence of π-π-stacking and alignment. In principle this is a lucky case. If the dimer formation can be prevented by any other space-filling procedure, then the ZnPc cores should generate alignable π-stacks of longer correlation length. Therefore, we assumed that mixtures of compound **2** and **3** would lock the ZnPcs in the center of the columns analogous to a ball detent mechanism, used macroscopically to fix metal pieces reversibly to defined positions (Figure 3A).

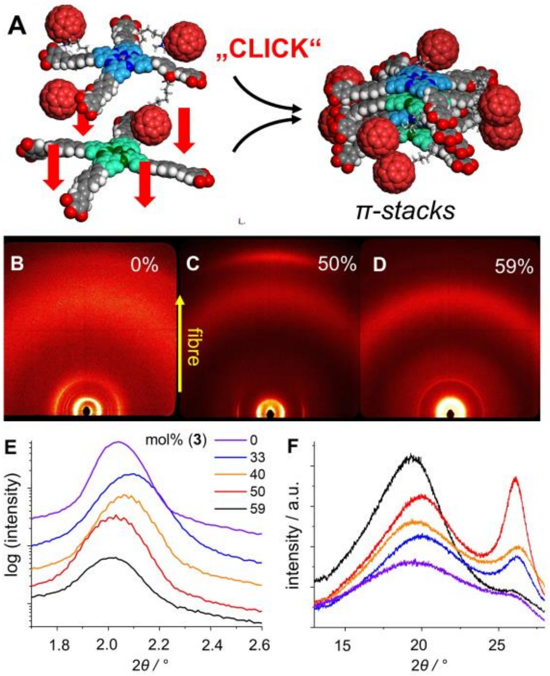


Figure 3. A: Click process by a ball detent mechanism (chains are omitted for clarity). B-F: XRS study. WAXS pattern at 220 °C of **2** (B), mixture with 50 mol% **3** (C) and 59 mol% **3** (D). Comparison of the positions of 10 reflections (E) and the WAXS region (F) for mixtures with increasing mole fraction of compound **3** given in mol%.

Figure 3 shows the XRS results from extruded fibers of a series of mixtures containing different mole fractions of **3** (0.00, 0.33, 0.40, 0.50, 0.59). The WAXS diffraction patterns at 220 °C clearly highlight the strong π-stacking signal and the rather good alignment along the fiber for the intermediate mole fractions (0.33-0.50, Figure 3B, Figure S10). The parent compound **2** (Figure 3B) and an excess of the sterically overcrowded compound **3** (Figure 3D) result in the loss of alignment and the longer π-stacked aggregates. This confirms clearly the concept of the supramolecular “click mechanism”. The temperature-dependent XRS of the 1 : 1 mixture (Figure S11) reveals that the molecules in the highly viscous fibers extruded at 170 °C are still not fixed together, but transform to the highly ordered and aligned columnar phase only above 190 °C. This “Click” process in the mesophase can be followed by DSC (Figure S8). Obviously the increasing mobility starting at 190 °C allows the molecules to arrange in the ordered LC phase accompanied by a characteristic weak endothermic signal. The alignment and order do not change after the first heating process and the DSC remains silent in the following cycles. This process is reversible, since the self-assembled mixture can be separated in its components by chromatography (Figure S9). The diffraction patterns of the materials with intermediate mole fractions consist of the equatorial reflections, which can be attributed to the 2D hexagonal packing of columns. The *a* parameters are increasing from 48.2 Å to 50.0 Å with the increasing mole fraction of **3** from 33-50 mol% (Figure 3E). This is in good agreement with fullerenes filling the free space between the arms, displacing other molecular building blocks to the periphery. The halo at 4.5 Å can be attributed to the average distance of hydrocarbons and the strong signal at the meridian corresponds to the π-π distance (3.4 Å). A set of two diffuse off-meridional signals points to an additional periodicity along the columns (Figures 2F,G inset). The latter intensities are most prominent for the 1 : 1 mixture. Analysis of the off-meridional reflections revealed that these signals are positioned at a layer line corresponding to a periodicity of 27.2 Å along the *c*-axis. With an experimental density of 1.28 gcm^{-3} four molecules of each **2** and **3** fill this columnar stratum. Thus 4 x 4 fullerenes must be assembled and owing to the molecular structure, it is reasonable to assume four strands of four fullerenes each. With a van der Waals diameter of a single fullerene of 10.3 Å the total length of four fullerenes in a chain is 41.2 Å. Consequently, the fullerenes must be strongly intercalated in the columnar repeat of 27.2 Å. In order to generate this periodicity continuously along the column, optimize the nanosegregation and avoid steric repulsion a helical arrangement is the most reasonable assumption. Dense helical packing of fullerenes depends on various geometrical parameters, e.g. the number of fullerenes in the helical pitch and thus the height *h* available for a single sphere along *c* and the rotation about the helical axis without losing the contact to the neighboring fullerene. These parameters determine the radius of the helical strand, which must be larger than the radius of the ZnPc core (approx. 8 Å) and cannot strongly exceed the radius of the column (approx. 25 Å). Furthermore, the symmetry of compound **3** allows only for the generation of a quadruple helix, thus the strongest X-ray intensities are expected to be on the fourth or eighth layer line.[17] The best agreement with the experimental diffraction pattern was obtained assuming a helical pitch and repeat along the *c*-axis of 217.8 Å. Then 64 phthalocyanines (128 fullerenes) pack in this giant unit cell with a distance of 3.4 Å and four helical fullerene strands lock (“click”) the aromatic discs to the column center. For steric reasons only 25 fullerenes from 32 can be assembled in a single helical strand while seven fullerenes are distributed randomly to vacancies in the interior of the column. After geometry optimization a 25_1 quadruple helix emerges (Figure 2K), which can be regarded as a snapshot of the LC assembly. The radius of the ideal 25_1 fullerene helix (26.2 Å) without steric congestions would be slightly larger than the experimental columnar diameter. As a consequence, the helices of different columns intersect (Figure 3I yellow arrows) and the helices are slightly deformed. This results in an additional nanosegregation and the formation of a fullerene network. All ZnPcs are forced to be in the center of the column in the regular π-stack, the shape-persistent oligo(phenyleneethenylene), defining the size of intrinsic free space, are placed helically in between the fullerenes, while the spacers, oligo(ethyleneoxy) chains and in total 4 x 7 = 28 residual fullerenes fill the remaining void. This model is confirmed by the simulated 2D fiber diffraction pattern showing all main features which are in agreement with the experimental results (Figure 2F inset).

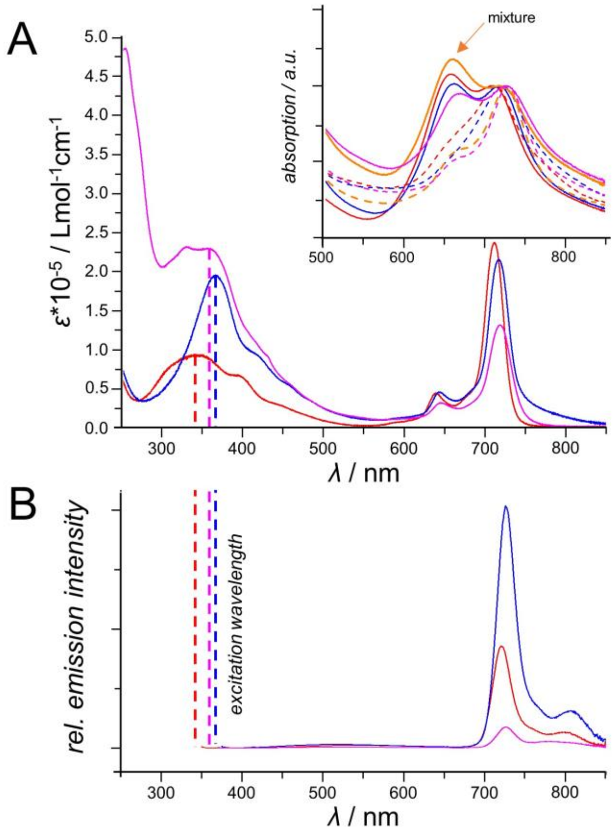


Figure 4. UV/vis absorption (A) and fluorescence spectra (B) of **1** (red), **2** (blue) and **3** (magenta) in THF. The inset in (A) shows the absorption spectra of spin-coated thin films as prepared (dashed line) and annealed at 220 °C solid line, normalized to the long wavelength absorption maxima. For comparison the spectra of the 1 : 1 mixture have been visualized.

The UV-Vis-spectra of the target molecules in $CHCl_3$ reveal almost as simple superpositions of the different individual building blocks (Figure 4). The ZnPc stars exhibit the Soret band at 396 nm (**1**) and 415 nm (**2**) and the Q-band with a maximum at 712 nm (**1**), 717 nm (**2**) and are superimposed by the oligo(phenyleneethenylene) absorptions with maxima at 339 nm for the short arm derivative **1** and 365 nm for the longer arm derivative **2**. Obviously, there is a small electronic effect of the different conjugated arms on the ZnPc absorption and vice versa. The molecule with four additional fullerenes possess further maxima at 254 and 330 nm, which can be attributed to the fullerene absorptions. The inset in Figure 4A highlights the normalized absorption spectra of spin-coated films as prepared and annealed at 220 °C in the range of the Q-band. The as prepared thin films resample the solution spectra but show the typical broadening of a solid. The annealed samples exhibit a new, blue-shifted band reminiscent for the coplanar stacking of H-aggregates.[18] This is most pronounced for the 1 : 1 mixture, which supports the favorable aggregation procedure by the Click process. The concentration corrected emission spectra in Figure 4B reveal exclusively the emission of the ZnPc Q-band, which is increasing with the increasing extinction coefficient of the conjugated arms and the efficient overlap of their emission spectra with the Soret band of the phthalocyanines. The frequently intense emission of the conjugated stilbenoid oligomers is completely quenched pointing to an effective energy transfer to the ZnPc moiety. Consequently, the molecules exhibit all features of an antenna system, which will be favorable for future photovoltaic materials. For the fullerene derivative also the ZnPc emission is efficiently quenched. Fluorescence spectroscopy with the thin film of the mixture reveals a complete absence of light emission pointing to the permanent presence of fullerenes close to the ZnPc in the LC state and a quantitative quenching process. A transient femtosecond spectroscopy study in solution and thin film revealed that fullerene anions and ZnPc cations are generated with a life time in the nanosecond range (Figure S17).[19]

In conclusion, the design of oligo(phenyleneethenylene) ZnPc star mesogens was highlighted – one which provide intrinsic void space and one which is sterically overcrowded with fullerene guests. While the mesogen without fullerenes is able to compensate the void by dimer formation the fullerene derivative is not liquid-crystalline. However, the 1 : 1 mixture of both reveal the formation of a highly ordered LC donor-acceptor system by a kind of ball detent mechanism, which we call a mechanical supramolecular “CLICK” procedure. Processes using the filling of voids are omnipresent in nature (e.g. function of enzymes) but here this strategy is used for the first time intentional to stabilize and organize a donor-acceptor system side by side in a single column. The conjugated arms are not only steric parts creating space but are building blocks of an antenna system transferring energy to the central phthalocyanine. This leads eventually to a charge separation providing ZnPc radical cations and fullerene radical anions. Thus this molecular system may become a promising organic photovoltaic material, if the columnar mesophases can be oriented homeotropically between two electrodes. These investigations are currently in progress.

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Keywords: Liquid Crystal • Donor-Acceptor Dyad • Supramolecular Click procedure• Columnar Phase • Helical packing

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[†] Footnote: M. L. and M. D. are responsible for synthesis, LC studies, absorption, emission spectroscopy and writing of the manuscript. M. H., A. S. and Ch. L. are responsible for the measurement, analysis and interpretation of femtosecond spectroscopy.

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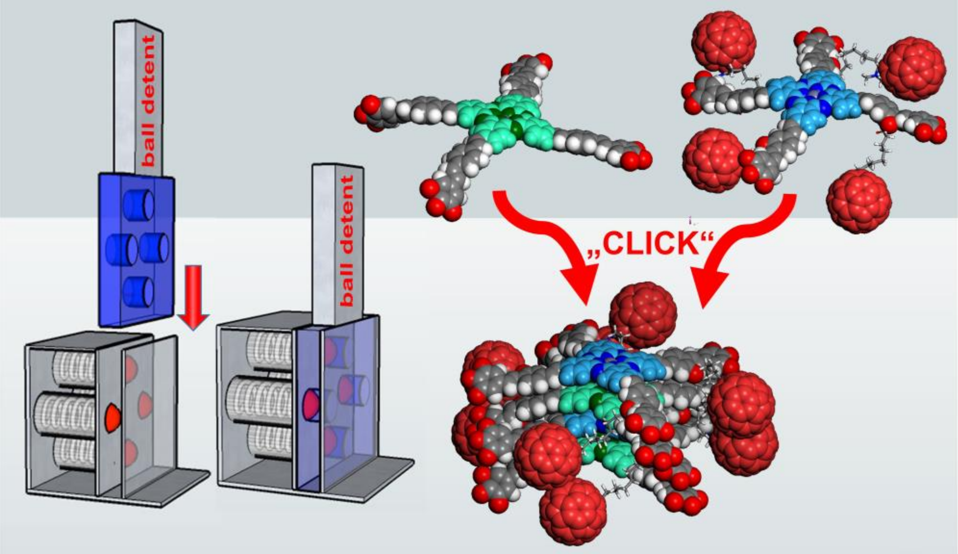

Only a Click Away: A supramolecular CLICK procedure leads to a helical columnar liquid-crystalline Donor-Acceptor separated antenna system by a molecular ball detent mechanism.