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Polarized Fluorescence from Single Stopcock Molecules at Channel Entrances of an All-Organic Host−Guest Compound

Anna M. Chizhik,[†] Ricarda Berger,[‖] Alexey I. Chizhik,[†] Alexey Lyubimtsev,[‡] Lucas Viani,[§]
Jérôme Cornil,[§] Sebastian Bär,[†] Michael Hanack,[‡] Jürg Hulliger,[*,‖] Alfred J. Meixner,[*,†]
Hans-Joachim Egelhaaf,[†,⊥,▽] and Johannes Gierschner[*,†,#]

[†]Institute of Physical and Theoretical Chemistry and [‡]Institute for Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

[§]Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc 20, B-7000 Mons, Belgium

[‖]Department of Chemistry and Biochemistry, University of Berne, Freiestrasse 3, CH-3012 Berne, Switzerland

[⊥]Christian-Doppler-Laboratory for Surface Optical Methods, Johannes-Keppler-University, Altenbergerstr. 69, A-4040 Linz, Austria

[#]IMDEA Nanoscience, UAM, Module C-IX, third Level, Av. Tómas y Valiente, 7, Campus Cantoblanco, E-28049 Madrid, Spain,

Supporting Information

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Host−guest compounds (HGCs) have gained considerable interest in the past few years, since they allow for the preparation of dye systems in well-defined geometries.[1−3] The HGC approach provides control over the interactions between chromophores, thus preserving their optical properties. In the case of *inorganic* zeolite-based HGCs, chromophores are incorporated into the host by diffusion from the gas phase or from solution.[2] To avoid out-diffusion of guest molecules, the zeolite channels are closed by so-called stopcock molecules, which consist of two covalently linked moieties. One of the moieties enters the zeolite, while the other one is too large to enter and thus closes the channel entrance.[2,4] Stopcocks may be used to provide HGCs with additional photophysical features such as efficient directed energy transfer to/from the channel ends, thus making HGCs suitable as photon harvesting antenna systems.[2] Among *organic* channel-forming host systems, perhydrotriphenylene (PHTP) has received special attention.[3,5,6] Upon cocrystallization with rod-shaped guest molecules, parallel stacks of PHTP molecules form nanochannels with diameters of about 5 Å, in which the guests are colinearly aligned. An interchannel distance of 15 Å ensures electronic separation of the chromophores.[3,5] PHTP-based HGCs were intensively investigated in the past few years in particular with respect to their potential for long-range energy transfer.[7,8] In contrast to the inorganic HGCs, the channels of the organic host are only formed in the presence of the guest compound; they are completely filled with guests, and no cavities are found. Consequently, a strict one-dimensional collinear arrangement of guest molecules in close van der Waals distance are found, which makes them exciting systems for both fundamental studies and as novel candidates for material science due to optimized charge[9] and energy transport.[7,8] Here, we demonstrate a first example of all-organic functional PHTP-based HGCs, featuring channels which are closed by stopcock molecules. The stopcock consists of a tetraphenylporphyrin, substituted with a long alkoxy chain (SC-TPP; Figure 1b), which enters the channels of PHTP. The unambiguous proof of the closure is possible through the application of a polarized single molecule technique, which is able to distinguish between isolated molecules and aggregated species. To our knowledge, this technique is applied to a supramolecular system for the first time.

The properties of the *single stopcock molecules* were characterized in a polymeric matrix prior to inclusion, using confocal microscopy under azimuthally polarized laser-beam (APLB) excitation.[10] This technique converts the linear polarization of a Gaussian laser beam into an azimuthal one.[11] As a result of this transformation, the image of a single molecule consists of two lobes with a dark gap in between. This gap corresponds to the projection of the transition dipole moment (TDM) of the emissive state onto the electric field vector of the laser light beam. In our case, the electric field vector is parallel to the plane of the substrate on which the sample is placed. Calculations showed that any tilt of the TDM with respect to this plane will lead to a decrease of the detected intensity of the image.[12,13] The image in Figure 1a reveals significant differences between the emission intensities of different molecules, which are mainly related to the different tilts of the molecular TDMs with respect to the sample surface. One of the molecules (at the bottom-left corner) shows the effect of sudden bleaching which proves the emitters to be single molecules. Furthermore, the APLB method might help to identify aggregation of molecules, even if the distance between them is much smaller than the resolution limit of the microscope, because molecular aggregates consisting of translationally nonequivalent molecules (e.g., disordered molecular clusters) do not exhibit the two lobe pattern.

To determine the orientation of the TDM against the alkyl tail, gas-phase structure and electronic properties of SC-TPP were investigated by (time dependent) density functional theory ((TD-)DFT) calculations; see Figure 1b. The phenyl rings are strongly twisted against the porphyrin core by $\theta_1 = 73°$ (with a

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small barrier of 0.7 kJ/mol at θ_1 = 90°; the barrier at 0° is far above kT, due to strong steric hindrance). The TDMs of the transitions from the ground state to the states S_1 (with an energy of E = 1.84 eV and an oscillator strength of f = 0.06) and S_2 (E = 1.96 eV, f = 0.16) are perpendicular to each other, pointing through the opposite amine and imine functionalities of the SC-TPP core, respectively. Upon introducing the alkoxy substituent into one of the phenyl groups, the TDMs of the first two states are slightly tilted by 1° and 5° within the plane of the TPP core. Rotation of the alkyl chain around the $C_{phenyl}-O$ bond results in two energetically equivalent conformations of SC-TPP at torsion angles of θ_2 = 0° and θ_2 = 180° (with respect to the plane of the phenyl ring). The rotational barrier of 15 kJ/mol at θ_2 = 90° between these two conformations is well above kT, so that the $O-C_{alkyl}$ bond is preferentially found in a plane perpendicular to the TPP core. Rotation of the alkyl chain around the $C_{alkyl}-O$ bond is almost unhindered at room temperature, having a barrier of only 1.2 kJ/mol at 32° with respect to the *trans*-configuration.

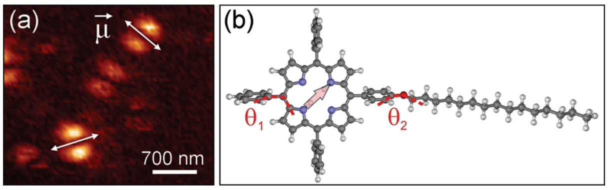

Figure 1. (a) Fluorescence microscopy image of six isolated TPP-SC molecules in PMMA, excited by APLB. Arrows indicate the orientation of the TDM (S_0-S_1) projection onto the sample surface. (b) DFT optimized geometry of TPP-SC. The arrow indicates the direction of the TDM; θ_1 is the tilt angle of the phenyl ring plane against the plane of the TPP core while θ_2 is the torsion angle between the plane of the phenyl ring and the $O-C_{alkyl}$ bond.

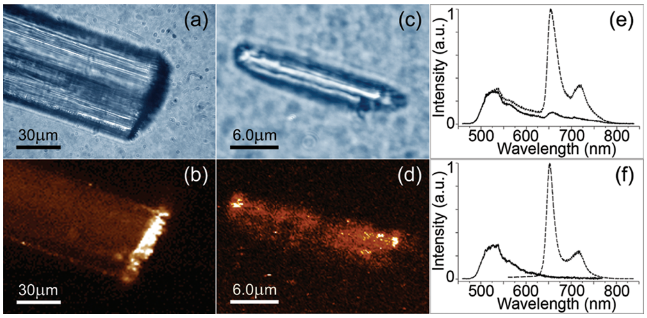

Figure 2. Optical (a, c) and fluorescence images (b, d) of a large (a, b) and a small (c, d) PHTP crystal with included stopcock (SC) molecules. (e) Normalized fluorescence spectra acquired at the end (dashed curve) and at the middle part (solid curve) of a crystal. (f) Emission spectra of SC molecules in PMMA (dashed curve) and of a stopcock-free PHTP crystal (solid curve).

PHTP-4,4′-dibromobiphenyl (DBBP) crystals without stopcock molecules were imaged by a digital optical microscope. They were found to be between 3 and 50 μm in diameter (0.1 to 2 mm in length, i.e., along the *c*-axis of the crystal). The channel ends show a certain distribution in space along the *c*-axis, with some of the channel entrances being dislocated up to several tens of micrometers from the crystal basis. A weak uniform background fluorescence signal is detected (Figure 2f) whose spectrum is identical to that of pure PHTP powder.

PHTP-DBBP crystals with stopcock molecules (PHTP-SC) were investigated by recording optical (Figure 2a,c) and fluorescence (Figure 2b,d) images. Strong fluorescence is emitted from the bases of the crystals, whereas the prism faces exhibit significantly lower intensity. This is quantified by the line scans in Figure 3a,b, which confirm that the emission is concentrated at the channel ends. Light guiding effects can be excluded as a reason for this observation, because inclusion compounds only with chromophore-filled channels but without stopcock molecules (which also should show light-guiding) did not show enhanced emission from the crystal ends.[14] Further evidence for the concentration of stopcocks at the channel ends arises from the comparison of the line scans through the crystals with low and high loading of the stopcock molecules (Figure 3). In crystals with low loading of fluorophores, the emission is limited to the channel ends (Figure 3a,b). For crystals with high loading, where all outer surfaces are covered by adsorbed fluorophores, the intensity profiles are homogeneous along the crystal axis (Figure 3c,d). Moreover, z-scans through the crystal base (not shown) reveal an increase of fluorescence intensity when going from the bottom toward the central axis of the crystal. Even after thorough washing of the crystals, adsorption might still occur at cracks present at the surface as demonstrated by the fluorescence image of a small crystal (length ca. 20 μm) with a rather inhomogeneous and rough surface structure (Figure 2c,d). However, the effect is rather minor as shown by the comparison of the fluorescence spectra in Figure 2e, demonstrating the background emission from the middle of the crystal which essentially corresponds to the emission of pure PHTP (Figure 2f, solid line). In contrast, the emission from the end of the crystal originates mainly from TPP. It is worth noting that, even after washing, the stopcocks remain stacked in the channel ends, thus confirming a perpetual sealing of the channels by the bulky stopcocks.

More detailed information on the insertion of the stopcock molecules into the channels of PHTP is provided by the APLB technique described above, which yields the orientation of the porphyrin TDM (S_1) with respect to the axis of the channel into which the alkoxy tail of the SC-TPP is inserted. For SC-TPP molecules which are not included in the channels, a random distribution of TDM orientations is expected. Evaluation of the two lobe patterns (Figure 4) with respect to their orientation against the crystal axis yields a ratio of parallel to perpendicular orientations of the TDM's projections on the sample surface

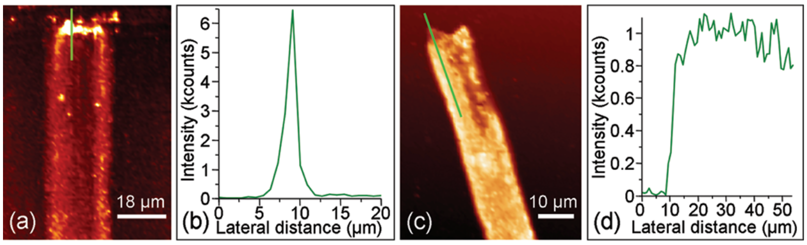

Figure 3. (a) Fluorescence image of a single PHTP crystal with included stopcock molecules; (b) emission intensity along the line indicated on the left; (c) fluorescence image of an a single PHTP crystal with stopcock molecules covering the surface of the crystal; (d) emission intensity along the line indicated on the left.

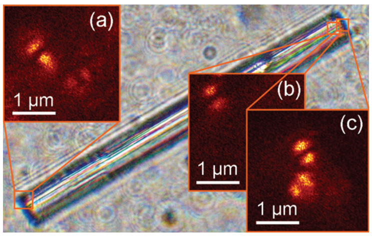

Figure 4. Fluorescence patterns of single stopcock molecules closing the channel entrances of PHTP crystal excited with APLB. The background is an optical image of the PHTP-SC-TPP crystal.

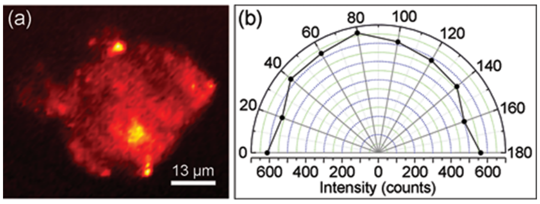

Figure 5. (a) Fluorescence image of the basis of the vertically oriented PHTP crystal with included SC molecules excited with an azimuthally polarized laser beam. The crystal axis is parallel to the exciting laser beam. (b) Intensity of the emission of the included SC molecules as a function of the rotation angle of the polarizer through which the emission is observed.

vs the crystal axis of about 2:1, whereas intermediate orientations of the patterns, that is, with both parallel and perpendicular components, are hardly observed.[15] This observation might be explained by the fact that the crystal basis is not a smooth planar surface but that some channels stick out more than others, as described above. TPP cores whose alkyl chains are inserted in protruding channels will attach face-on to the crystal basis. This leads to projections of the TDMs which are perpendicular to the crystal axis. TPP cores, whose alkyl chains are inserted in channels which are surrounded by protruding ones, will adsorb to the side walls of adjacent protruding channels. The resulting projections of the TDMs will be preferentially parallel to the crystal axis. For a parallel orientation of the crystal axis with respect to the laser beam (i.e., perpendicular to the substrate surface), we observed completely depolarized emission (Figure 5) showing the absence of one particular preferable direction of the SC molecules TDMs projection on the surface perpendicular to the crystal axis. According to expectations, this result demonstrates that the SC molecules, attached face-on to the crystal basis, can possess any projection of the TDM on the surface, perpendicular to the crystal axis.

In conclusion, we have prepared the first example of an all-organic channel-forming host−guest compound where the channel entrances are closed by porphyrin based molecular stopcocks. As a result of the dense and homogeneous 1D collinear arrangement of guest molecules which can be realized in organic HGC, this novel stopcock system might open up new possibilities for external electric[9] and optical[4,5] addressing through efficient exciton injection/extraction from the active stopcock to dye molecules enclosed in the channels.[2,4] The localization of the stopcocks in the channel entrances was confirmed by a combination of quantum-chemical calculations with polarized single molecule fluorescence imaging techniques, which was demonstrated to be a powerful method for the investigation of supramolecular systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details on synthesis and characterization of SC-TPP, preparation of the HGCs, fluorescence spectroscopy, microscopy, and quantum-chemical calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Present Addresses

$^{\triangledown}$Konarka Technologies GmbH, Landgrabenstr. 94, D-90443, Nürnberg, Germany.

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