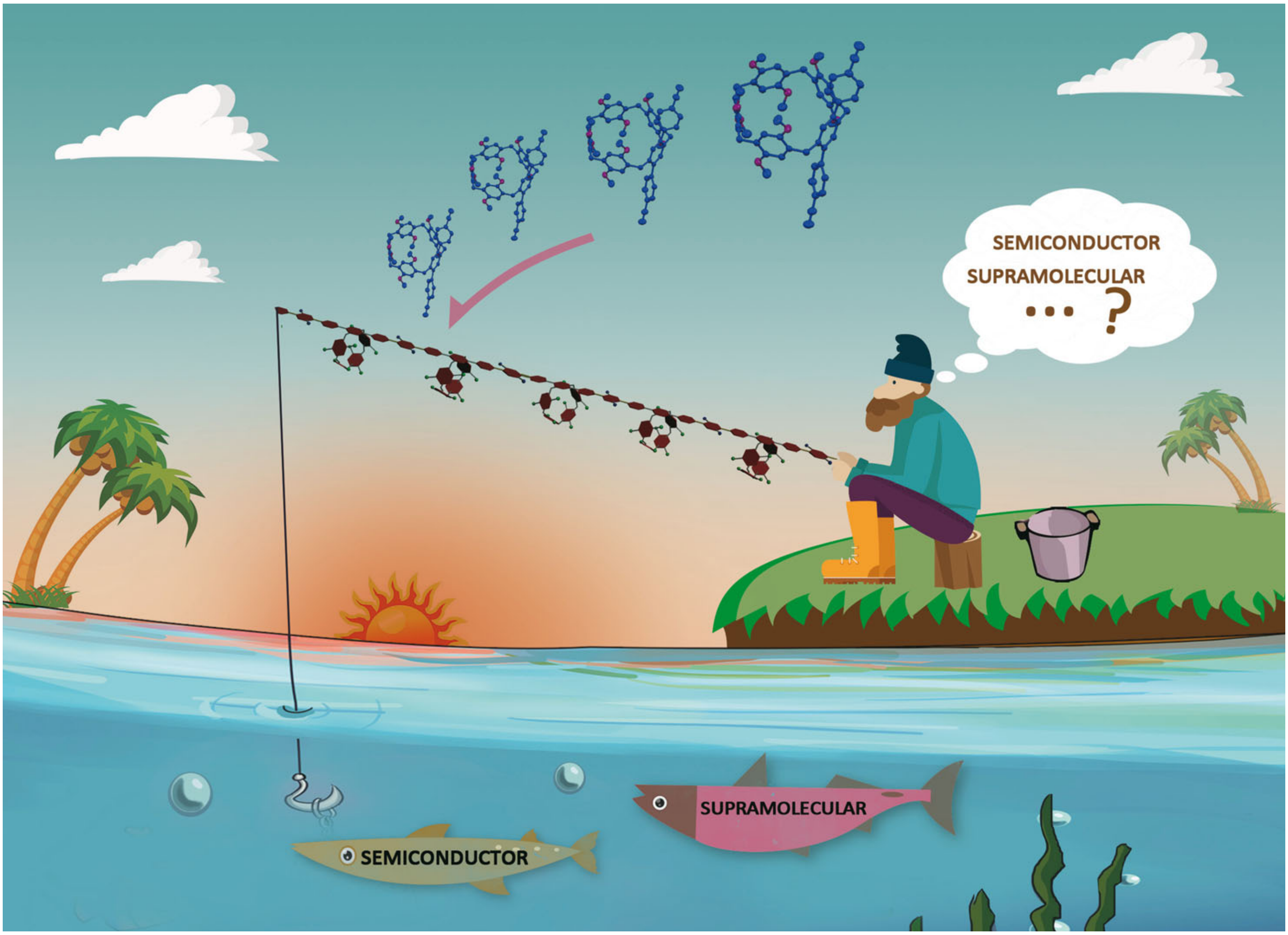

Showcasing research from Klaus Müllen's laboratory, Max-Planck-Institut für Polymerforschung, Germany.

A fishing rod-like conjugated polymer bearing pillar[5]arenes

A novel fishing rod-like conjugated polymer bearing pillar[5]arene has been synthesized and characterized. The new polymer has the features of both semiconductors and supramolecular structures, thus can potentially be used for electronic sensing devices.

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A fishing rod-like conjugated polymer bearing pillar[5]arenes†

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A novel diethynyl functionalized pillar[5]arene, that is a pentabenzenacyclodecaphane derivative, has been synthesized and polymerized with *p*-dihalobenzene to form a fishing rod-like conjugated polymer, where one of the benzenes in the pillar[5]arene rings is incorporated into a poly(arylene ethynylene) backbone.

Chemists can tailor conjugated polymers (CPs) for various physical and electronic properties by introducing functional groups,[1–5] such as macrocycles either as part of the polymer backbone or as substituents. *Via* integration of different kinds of macrocycles into conjugated polymer backbones, the polymers could be endowed with novel roles merging chemoreceptivity, electronics and supramolecular chemistry. Fig. 1 illustrates two modes for their incorporation into the polymer backbone. Swager and co-workers inserted calix[4]arene (at the upper rim) into thiophene-based polymers, such that the macrocycle forms a bridge, and obtained an electroactive zigzag structure (Fig. 1a).[6a] Alternately, Vigalok *et al.* reported a polymer incorporating only a single benzene ring of each tetrabenzenacyclodecaphane rings into the backbone, giving fluorescent materials that could detect gaseous nitric oxide *via* reversible complexation (Fig. 1b).[6b]

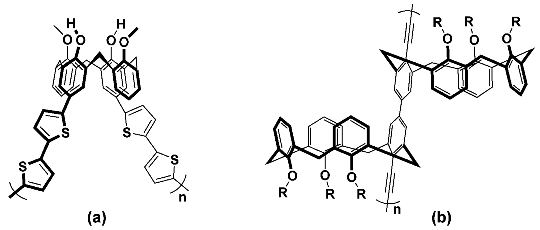

Fig. 1 Representative conjugated polymer adopting macrocycles as backbones.

Pillararenes, especially pillar[5]arenes (compounds **2–4**, Scheme 1), a new class of macrocycles, *i.e.* pentabenzenacyclodecaphanes, have attracted much interest recently,[7a] due to their facile synthesis as well as versatile nature as chemoreceptors. Different from the *meta*-bridged calixarenes, pillararene rings are formed by methylene bridges through *para*-phenylenes. Pillar[5]arenes are good host molecules for different electron-accepting guests or other neutral molecules, for instance dialkyl viologens,[7a] alkylated pyridiniums[7f] and *n*-hexane.[8a] Moreover, they can be easily functionalized especially on the benzene rings, rendering them to be promising vesicles,[8e] artificial transmembrane channels,[9b] nanotubes,[8d] nanoparticles,[8f] and other supramolecular systems for chemical and biological applications.[7–10]

Up to now there have been only a few examples of pillar[5]arene incorporated CPs, such as pillar[5]arenes as tethered side chain functionalized polyphenylethynylene,[9c] and the Zylon poly(*p*-phenylene-2,6-benzobisoxazole) derivative generated by the polymerization of one benzene unit in the pillar[5]arene monomer.[7g] Herein, we synthesized a novel bifunctional pillar[5]arene monomer bearing two alkynyl groups, from which a new pillar[5]arene-based conjugated polymer (**1**) was prepared by the Sonogashira polycondensation, as illustrated in Scheme 1.

Compound **4** with two hydroxyl groups was treated with trifluoromethanesulfonic anhydride to give ditriflated pillar[5]arene (compound **3**).[7b] Subsequently, the Pd-catalyzed Suzuki–Miyaura cross-coupling of **3** with trimethyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)silane **6** followed by removing the trimethylsilyl groups led to the targeted pillar[5]arene **2** containing two ethynyl groups for polymerization. The structure of **2** was confirmed by ^{1}H, ^{13}C, 2D NMR and high resolution mass spectrometry (Fig. S2–S7, ESI†).

Single crystals of **2** were obtained by the diffusion of MeOH into a dichloromethane solution of **2**. The X-ray crystallographic analysis indicates the presence of enantiomers in the unit cell (Fig. 2). The formation of *pS* and *pR* enantiomers is due to the molecule's planar chirality—the phenylene units of the

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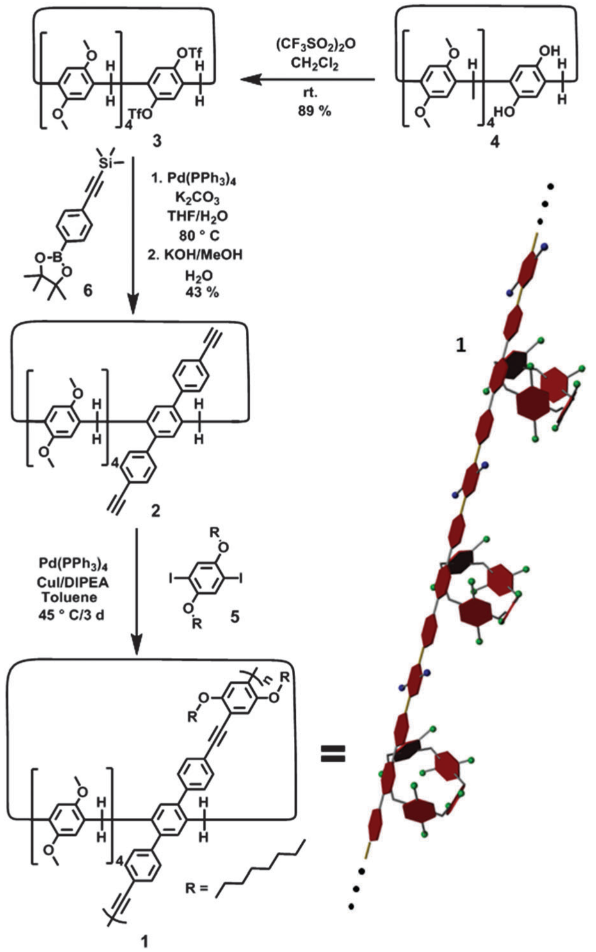

Scheme 1 Synthesis of the pillar[5]arene-based conjugated polymer (**1**).

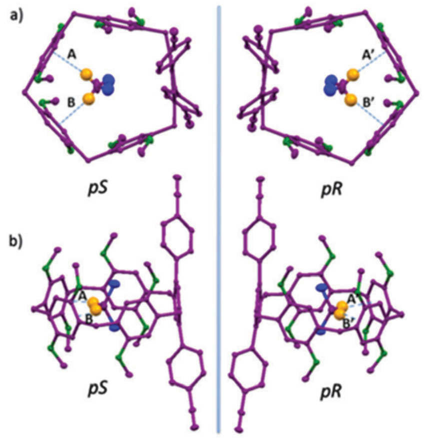

Fig. 2 Crystal structure of compound $\mathbf{2}\supset CH_2Cl_2$ which displays planar chirality. Hydrogens on **2** omitted for clarity. (a) *pS*-and *pR*-conformations of $\mathbf{2}\supset CH_2Cl_2$ (top view); (b) (side view). The blue dotted lines indicate the C–H···π interactions. Color codes: carbon, purple; hydrogen, orange; oxygen, green; and chlorine, blue.

parent dimethoxypillar[5]arene can rotate around the methylene bridges, affording two conformations (*pS* and *pR*), which however easily interconvert in solution. Nevertheless, the bulky 4-ethynylphenyl groups in **2** prevent the rotation of the units and thus inhibit the interconversion between the two conformations. As a consequence, the *pS* and *pR* enantiomers are stabilized.[7d] It is also noticeable that a dichloromethane molecule is encapsulated in the cavity of each molecule of compound **2**. Particularly, the distances between the hydrogen atoms of the dichloromethane molecule and the corresponding phenyl ring of pillar[5]arenes (the bonds A, B, A′ and B′ in Fig. 2) is only 2.71 Å, which indicates the C–H·π interactions between dichloromethane and the cavity of **2** (see the blue dotted lines in Fig. 2). This is similar to the case of mono-octyl-substituted copillar[5]arene in the solid state.[8a]

In order to polymerize **2** under Sonogashira conditions, we prepared monomer **5** as the dihalo-aromatic comonomer (Fig. S8, ESI†). After combining **2** and **5** with a catalytic amount of $Pd(PPh_3)_4$ and CuI in diisopropylamine–toluene, the crude polymer could be easily purified by precipitation from dichloromethane by addition of methanol to give the target polymer **1** as a yellow solid (94% isolated yield).

According to gel permeation chromatography (GPC), the relative number-average molecular weight (M_n) of CP1 was about 16 kDa with a polydispersity index (PDI) of 3.82 (THF eluent, polystyrene standards, Fig. S10, ESI†). This corresponds to an average of thirteen repeat units in the polymer backbone. Polymer **1** is highly soluble in common organic solvents ($CHCl_3$, CH_2Cl_2, THF, and toluene) allowing thorough characterization by ^1H NMR spectroscopy. The ^1H NMR spectrum of **1** indicated that proton signals assigned to pillar[5]arene benzene rings and methoxy groups shifted upfield and downfield,

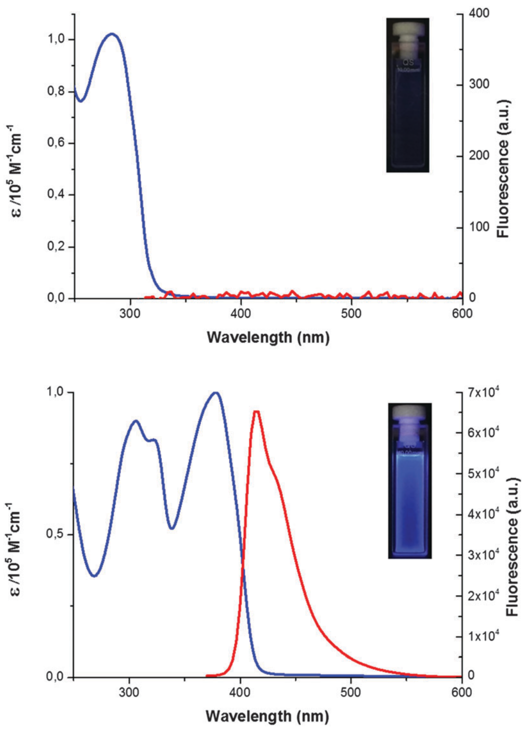

Fig. 3 UV-visible absorption (blue line) and fluorescence (red line) spectra of monomers **2** (top, 10^{-5} M) and **1** (bottom, [RU] = 10^{-5} M, chloroform).

Table 1 Molecular weight and optical properties

			Solution ($CHCl_3$)		Film	
	M_n (kDa)	PDI	Abs λ_{max} (nm)	Em λ_{max} (nm)	Abs λ_{max} (nm)	Em λ_{max} (nm)
1	16	3.8	306, 378	416	303, 377	429

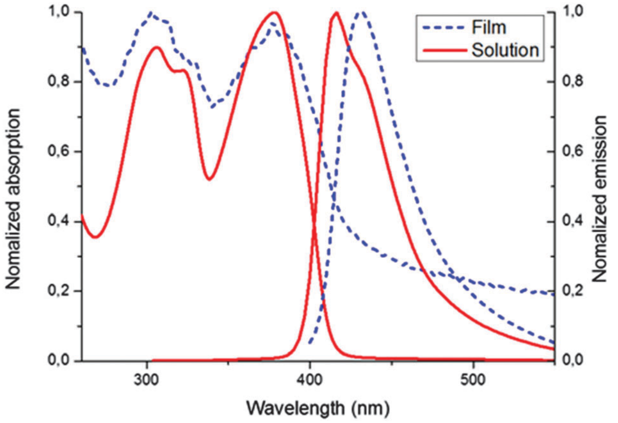

Fig. 4 Normalized absorption and emission spectra of **1** in $CHCl_3$ (red/solid) and in thin film (blue/dashed).

respectively, compared with those of monomer **2** (Fig. S9, ESI†). The polymer structure is further supported by the matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) spectrum, which exhibited a series of peaks, regularly separated by the molar mass of the repeat unit (1220, Fig. S11, ESI†). All the results above confirmed the successful synthesis of **1** bearing pillar[5]arenes in the conjugated backbone. Polymer **1** can be viewed as a fishing rod-like conjugated "hydrocarbon nanotube"[6b] – the conjugated backbone is the rod and the pillar[5]arene units are the guides arranged along the underside of the fishing rod (Scheme 1).

The UV-visible absorption and fluorescence spectra of polymer **1** were compared to those of monomer **2** (Fig. 3). The extended conjugation had a profound effect on the UV-visible and fluorescence properties of the pillar[5]arene compound (Table 1)—monomer **2** has absorption maximum at 284 nm, while **1** has absorption maxima at 306 and 378 nm with a significant bathochromic shift of 94 nm. On the other hand, monomer **2** is hardly fluorescent, but **1** is highly blue fluorescent with emission maximum at 416 nm, as a result of the formation of the conjugated backbone.

Compared to the adsorption spectrum in solution, the broader adsorption spectrum of **1** in the film indicates that aggregation occurs in the solid state (Fig. 4). Furthermore, the emission peak of **1** shows a noticeable red-shift (~13 nm) in the solid state relative to the solution spectrum.

In summary, we have described an efficient pathway towards a new bifunctional pillar[5]arene monomer bearing two alkynyl groups for easy and efficient polymerization under Sonogashira conditions to achieve a fishing rod-like conjugated polymer. The new polymer has the features of both semiconductor polymers and supramolecular structures. Further investigation of electronic sensing devices is underway in our laboratory to provide application information of polymer **1**.

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