Energy-Transfer Systems

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Exciton Accumulation in π-Conjugated Wires Encapsulated by Light-Harvesting Macrocycles**

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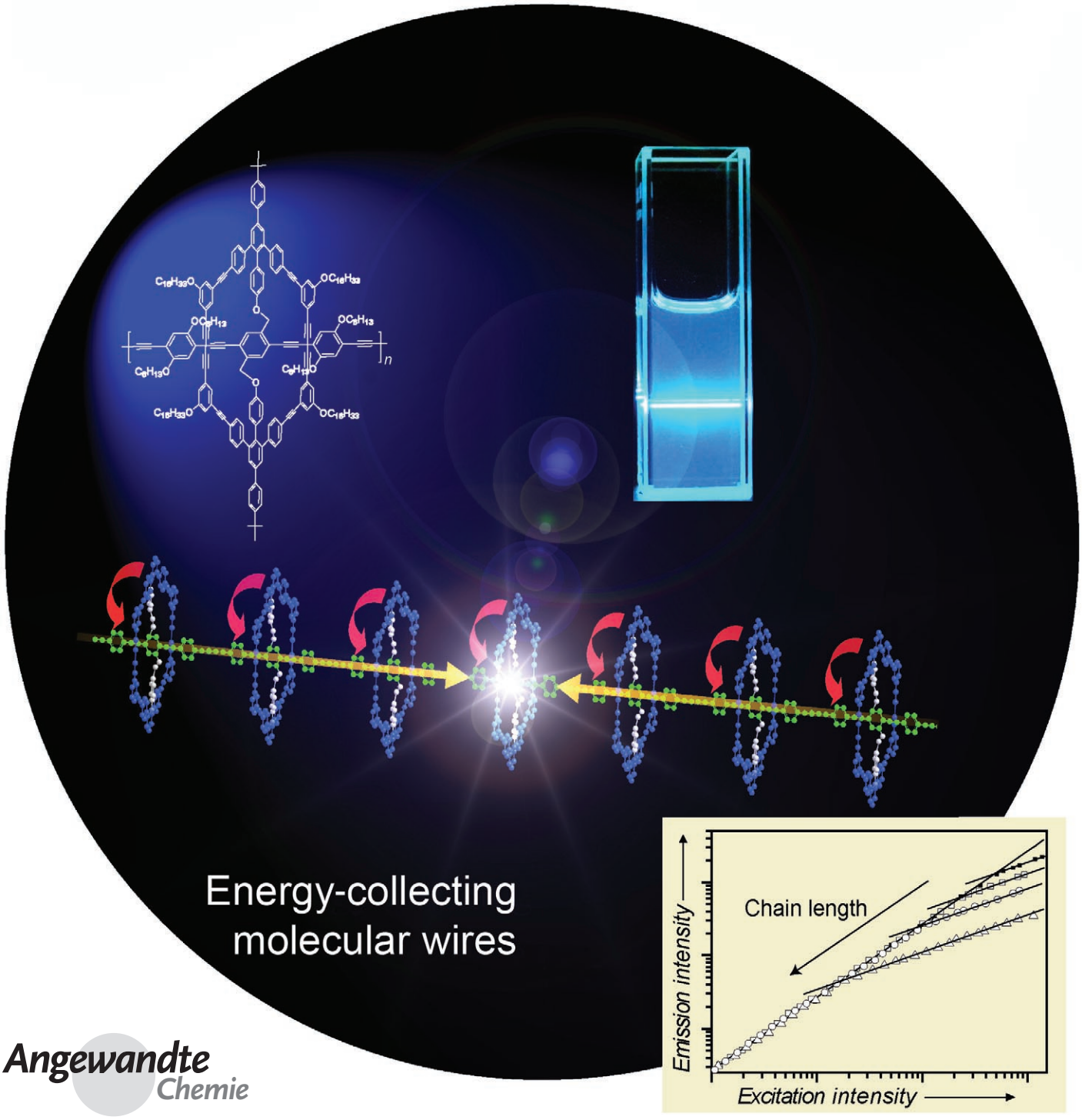
Dedicated to Professor Klaus Müllen on the occasion of his 60th birthday



The ability to absorb light energy and convert it into a molecular redistribution in charge density is fundamental to nature and life itself. To do this efficiently, a spatial and energetic separation of the light-absorbing unit from the part of a complex which actually performs the useful function—the reaction center—is required.[1] While there are numerous examples of synthetic and structural approaches to mimic light harvesting,[2–5] to put the funneled and concentrated excitation energy to work has only rarely been considered.[3c] Light-harvesting supramolecular assemblies of chromophores, including arrangements containing shape-persistent macrocycles, have recently attracted considerable interest.[6] However, covalently bound, polymeric multichromophoric systems generally offer much greater stability than supramolecular complexes which makes such materials more appealing for device applications. There are many examples in which the concentration of excitation energy, as sketched in Figure 1, is desirable: photovoltaics necessitate a spatial separation of absorbing and charge-separating units; lasing applications require large excitation densities in particular molecular units which can be reached by cascading the excitation energy;[7] and novel photochemical sensors may exploit intramolecular excitation-energy transfer (EET) in a cascade arrangement to amplify the overall sensitivity.[8]

Herein, we describe a new approach to π-conjugated wires encapsulated in a "tube" of covalently bound shape-persistent macrocycles, which enable both light harvesting and concentration of excitation energy within the core of the molecule. We chose poly(phenylene-ethynylene-butadiynylene) as a model wire system owing to the substantial persistence length and high structural rigidity.[9] The synthesis of the "ring polymer" **1** is illustrated in Scheme 1 along with the structures of the corresponding model compounds, polymer **2** and ring **3**. The synthesis of the macrocycle in **1** and **3** is based on the intramolecular coupling of appropriate ring precursors covalently bound to a template.[10] Tetraacetylene **4**, obtained from the corresponding phenol and 2,5-diiodo-1,4-bis(bromomethyl)benzene,[11] was cyclized under pseudo-high-dilution conditions to give macrocycle **5** in good yield. Hagihara–Sonogashira coupling of **5** with 2.5 equivalents of **6** and fluoride-induced desilylation of **7** gave bis-

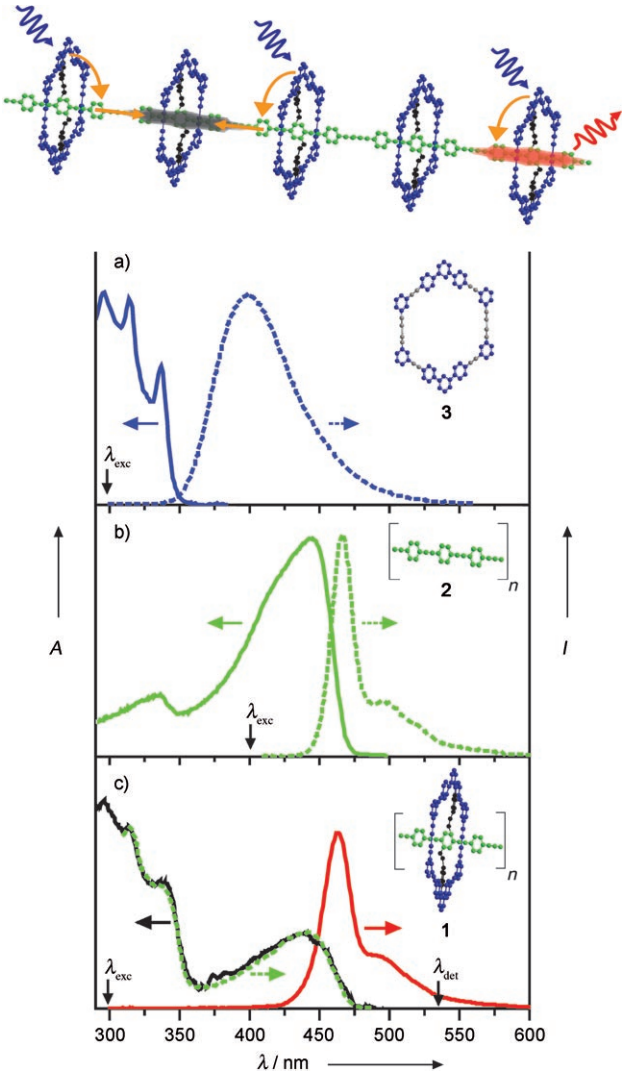


Figure 1. Schematic of the light-harvesting properties of poly(*para*-phenylene-ethynylene-butadiynylene) covalently encapsulated by conjugated macrocycles (i.e. **1**). The orange arrows indicate EET from the rings to the conjugated intraannular wire, which can lead to both single (red) or multiple, self-annihilating (black) excitation. a) Absorption (blue line) and fluorescence (dotted blue line; $\lambda_{exc} = 290$ nm) spectra of the macrocycle **3**. b) Absorption (green line) and fluorescence (dotted green line, $\lambda_{exc} = 400$ nm) spectra of the polymer **2**. c) Absorption (black line), excitation (dotted green line; $\lambda_{det} = 530$ nm), and fluorescence (red line, $\lambda_{exc} = 290$ nm) spectra of the ring polymer **1**. The features around 375 nm in the absorption spectra correspond to noise from the detector resulting from the extremely low solution concentration (absorption is less sensitive than excitation spectroscopy). All measurements were carried out on chloroform solutions.

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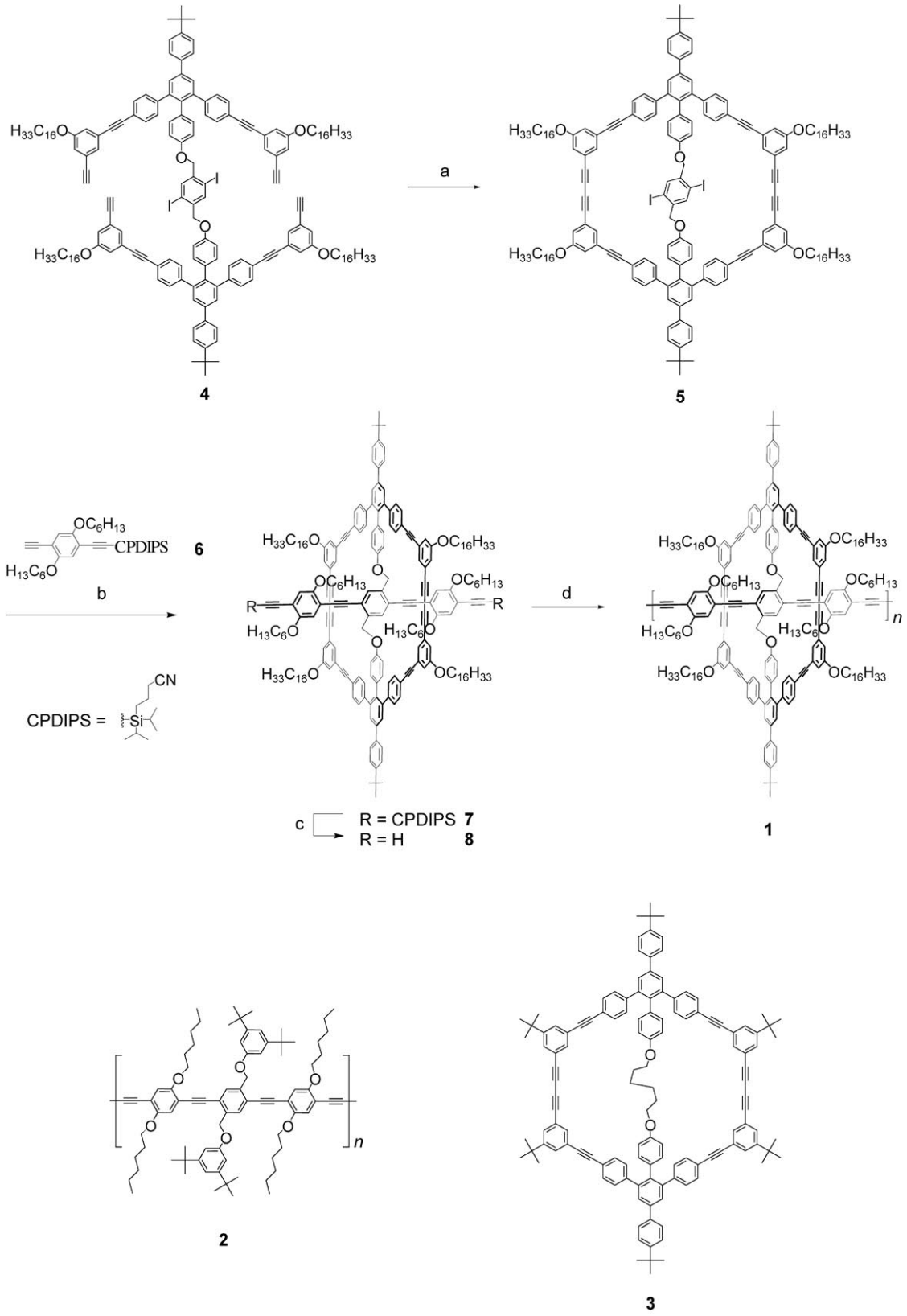

Scheme 1. Top: Synthesis of the ring polymer **1.** Reagents and conditions: a) CuCl, $CuCl_2$, pyridine, room temperature, 96 h, 90%; b) **6**, $[Pd(PPh_3)_2Cl_2]$, PPh_3, CuI, THF, piperidine, room temperature, 12 h, 73%; c) Bu_4NF, THF, room temperature, 12 h, 39%; d) CuCl, air, TMEDA, *o*-dichlorobenzene, 35 °C, 10 days. Bottom: Structures of **2** and **3**.

acetylene **8**.[12] The oxidative acetylene polymerization was performed under the conditions described by Havinga (CuCl, air, tetramethylethylenediamine (TMEDA), *o*-dichlorobenzene).[13] Ring polymer **1** is readily soluble in common organic solvents such as dichloromethane, chloroform, and THF. Gel permeation chromatography (GPC) analysis of **1** indicated a number-average molecular weight (M_n) of 33000 g mol^{-1} and a weight-average molecular weight (M_w) of 75000 g mol^{-1} (THF, polystyrene (PS) standard). GPC-resolved oligomers provided an indication for the accuracy of this analysis by showing good agreement between the GPC-determined and the expected molecular weight below 30000 g mol^{-1}.[14] The GPC analysis of **2** yielded an M_n value of 25000 g mol^{-1} and M_w value of 83000 g mol^{-1} (THF, PS standard).

We propose that stepwise coupling of **5** with **6** ensures that the phenylene-ethynylene moiety in **7**, **8**, and also in **1** penetrates the rigid macrocycle in an almost orthogonal orientation. As a result, the conjugated polymer **1** is molecularly threaded into a tube of macrocycles. Site isolation of conjugated polymers by polymerization of rotaxanes[4f] as well as the decoration of conjugated polymers with bulky (dendritic) side groups[4h] has previously been reported to reduce interchain interactions. However, the design principle of the ring polymer conjugate **1** is rather new: the steric demand of peripheral side groups should have only limited influence on the site-isolated polymer-chain conformation as the conjugated polymer is covalently encapsulated by the macrocycle "tube".[15] This is in contrast to dendronized polymers, in which steric interactions of the bulky side groups can perturb the electronic properties of the core.[4c]

Figure 1 shows absorption, photoluminescence (PL), and PL excitation (PLE) spectra of the ring polymer **1** and the reference compounds, polymer **2** and macrocycle **3**. The absorption for the ring polymer (black line) shows two distinct features peaking at 442 and 337 nm. It is approximately described by a superposition of the absorptions of polymer **2** (green line) and the bare macrocycle **3** (blue line). The emission of the bare macrocycle **3** (blue dotted line) is broad and overlaps the absorption of the polymer **2** completely so that resonant EET occurs by nonradiative dipole–dipole coupling. As a result, the PL of **1** is independent of excitation wavelength and identical to that of the core polymer **2** which suggests that EET is virtually complete. Consequently, the PLE spectrum (Figure 1c; green dotted line) under detection in the tail of the core emission at 530 nm closely follows the absorption spectrum of **1** and illustrates that the emission always occurs from the core, irrespective of the energy of the photon absorbed. Note that the ring dipole is evidently not completely orthogonal to the polymer dipole or else no EET could occur. A rough estimate of the Förster transfer rate yields near-unity transfer efficiency for an orientation only 3° off normal.

The absorption of the macrocycle–polymer system resembles a superposition of the absorptions of the constituent macrocycle and polymer. However, binding the macrocycle to the polymer could change the individual absorptions. Ultimate confirmation that EET does occur within the molecule comes from a temporal rise in the emission of the acceptor. Figure 2 shows the time-resolved fluorescence of **1** detected at

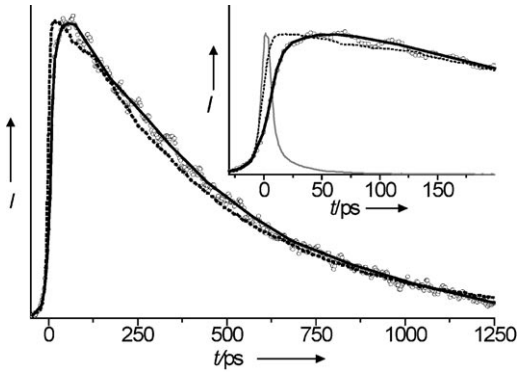

Figure 2. The dotted curve shows the decay of the polymer fluorescence under excitation at 415 nm, that is, corresponding to the absorption of the polymer. The rise in the emission in this case is comparable to the instrument response function (shown by the thin gray line in the inset). The solid line shows the polymer fluorescence measured under excitation of the rings at 300 nm (circles and solid line): the transient is described by the product of two single-exponential functions for the rise and the decay of the emission, providing a clear signature of EET from the outer ring to the intraannular polymer. The inset shows a closer view of the temporal region in which EET occurs from the rings to the core.

465 nm (core emission) using a streak camera with a temporal resolution of 4 ps. The material was excited at 415 nm (polymer absorption, dotted line) and 300 nm (ring absorption, solid line and gray points) by a frequency-doubled Ti:Sapphire fs laser. At 300 nm the ring absorbs approximately 13-times more than the polymer. Under excitation of the polymer, the luminescence rises within the instrument response. In contrast, when exciting at higher photon energy the PL does not reach its intensity maximum until 50 ps after excitation. This rise provides proof that the absorption spectrum of **1** does indeed originate from the two distinct species. The normalized transient PL intensity $I(t)$ under excitation of the ring is described by the product of a single-exponential rise and decay according to Equation (1).

$$I(t) = (1-e^{-t k_{EET}})\, e^{-t k_{polymer}} \quad (1)$$

The extracted EET rate $k_{EET} = 5.6 \times 10^{10}\ s^{-1}$ is much greater than the PL rates of the ring ($k_{ring} = 9 \times 10^{8}\ s^{-1}$) and of the polymer ($k_{polymer} = 1.8 \times 10^{9}\ s^{-1}$), respectively. The EET efficiency is almost unity ($\eta_{EET} = k_{EET}/(k_{EET}+k_{ring}) = 98.4\,\%$), in agreement with the aforementioned quantitative match of PLE and absorption spectra. Note that the bare polymer **2** with spectrally identical features decays slightly faster with $k = 2.4 \times 10^{9}\ s^{-1}$ (not shown). This rate increase is mirrored in the reduction in PL quantum yield. Polymer **2** also displays reduced photochemical stability. We attribute these differences to more facile defect formation and quenching of the excited state in the absence of the rings.[4c]

Our polymer light-harvesting system is rather different to most traditional dendrimer-based structures in that the multichromophoric core can potentially support multiple excitations.[16a,b] The presence of more than one excitation should allow the observation of exciton–exciton interactions such as

singlet–singlet annihilation within the core. The population decay rate dn/dt is described by Equation (2), where n is the

$$\frac{dn}{dt} = -\gamma_1 n - \frac{1}{2}\gamma_2 n^2 \quad (2)$$

exciton concentration and γ_1 and γ_2 are the inverse emission lifetime and the exciton–exciton annihilation rate, respectively.

For low excitation densities n (or pump intensities I_{exc}), the luminescence I_{em} is proportional to I_{exc}. Above a threshold, nonlinear interactions become significant with singlet–singlet annihilation[16c–e] providing an additional way of dissipating energy. The signature of this effect is that the pump power dependence of the luminescence drops from linear to square root.[16c]

To study exciton accumulation on the polymer core, polymer **1** was fractionated by GPC into three samples of different molecular weight (Figure 3a).[17] We measured the PL intensity as a function of pump power for the three samples and monomer **8** under excitation at 337 nm (constant optical density) using a nitrogen laser operating at 20 Hz repetition rate and 500 ps pulse length. At this wavelength, excitation occurs to over 80% in the rings. Figure 3b shows the emission versus excitation intensity on a double-logarithmic scale. The monomer **8** displays a linear relationship up to 5×10^6 W cm^{-2} pump power, and then turns to the expected[16c] I_{em} is proportional to $\sqrt{I_{exc}}$ dependence. As the chain length increases, the threshold power for exciton–exciton annihilation (which signifies the presence of at least two excitations on the molecule) drops approximately reciprocally with the length by a factor of 30 while the overall excitation density (absorbance and emission intensity) remains the same. This behavior demonstrates that accumulation of excitation energy occurs on the individual chains as sketched in Figure 1 and that the excitations are sufficiently mobile on the extended polymer to interact with one another. The monotonic decrease in threshold suggests that the scaffolded polymer is sufficiently rigid irrespective of chain length so that the two excitons required for an annihilation event can traverse the entire molecule.[17,18]

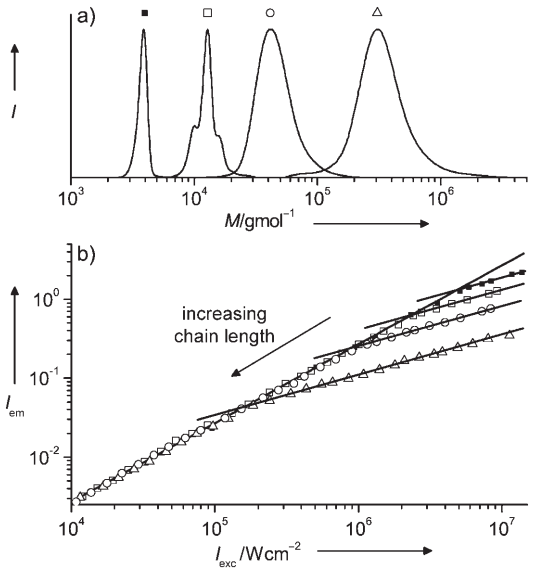

Figure 3. Exciton accumulation in the linear π system revealed by exciton–exciton annihilation and a resulting sublinear intensity dependence. a) GPC traces (UV detection) of the separated sample of **1** and the corresponding monomer **8** (from left to right): peak molecular weight (M_p) = 4×10^3 g mol^{-1}, polydispersity (D) = 1.01; $M_p = 13\times10^3$ g mol^{-1}, D = 1.04; $M_p = 43\times10^3$ g mol^{-1}, D = 1.13; $M_p = 310\times10^3$ g mol^{-1}, D = 1.30 (all determined using a PS standard). b) Plot of PL intensity as a function of excitation intensity on a double-logarithmic scale for the four samples of different chain length indicated in part (a). The material was excited in the absorption band corresponding to the rings at 337 nm. The straight lines indicate linear and square-root power dependencies.

In summary, we have demonstrated light harvesting in a covalently bound macrocycle–polymer complex. The ring templates bring together many of the advantages of dendronized polymers such as reduced intermolecular interactions and the potential for improving structural rigidity. In addition, the light-harvesting function combined with the multichromophoric nature of conjugated polymers provides a route to accumulating excitation energy within an individual molecule, rather than merely directing it. While we have demonstrated the effect of this accumulation in fluorescence, we hope to apply it in charge transfer, isomerization reactions, lasing, or EET-based sensing systems.

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[12] The use of the polar stable (3-cyanopropyl)diisopropylsilyl (CPDIPS) group at the acetylene simplifies the purification of **7**. A detailed description of this silylacetylene will be presented elsewhere.

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[14] GPC-resolved oligomers of **1** with a different degree of polymerization n allowed a direct comparison between the calculated (calcd) and the measured (obs) peak molecular weights (M_p). Data obtained versus PS calibration given in $g\,mol^{-1}$: $n=1$: M_p (calcd) $=3.7\times10^3$, M_p (obs) $=3.1\times10^3$; $n=4$: M_p (calcd) $=12.5\times10^3$, M_p (obs) $=13.0\times10^3$; $n=8$: M_p (calcd) $=25\times10^3$, M_p (obs) $=28\times10^3$.

[15] The reduced interchain interaction in **1** compared to **2** leads to different spectroscopic behavior in the solid state. Detailed investigations will be reported elsewhere.

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[17] We performed detailed single-molecule polarization anisotropy studies of the bare and the encapsulated conjugated polymers, which indicate that the encapsulated polymers are more extended than the bare chains and less prone to kinking. However, in view of the lack of suitable standards of rigid rod polymers for GPC, we note that the absolute values of the molecular weight of the polymers should be treated with caution at present. We are currently working on more accurate determinations of the molecular weight. While relative comparisons between different chain lengths are unproblematic (as shown in Figure 3), we refrain from making a direct comparison of the molecular weights of bare and encapsulated polymers. While the macrocycles do not appear to have an impact on the electronic properties of the polymer other than to improve photochemical stability, we anticipate that an enhancement of structural rigidity should facilitate exciton migration along the chain, a prerequisite for the interaction of excitons generated on different chromophores of the polymer.

[18] We refrain from attempting to calculate the precise number of excitons present per molecule for a given excitation density owing to the present uncertainty in determining the molecular weight accurately. Suffice it to note that the threshold for sublinear behavior should provide a signature of the presence of two excitons on the molecule. We expect the threshold for nonlinear interactions to be substantially increased in the bare polymer owing to the reduced exciton (PL) lifetime and the most likely decreased rigidity which should impede exciton mobility.

