Amphiphilic conjugated thiophenes for self-assembling antenna systems in water[†][‡]

Patrick van Rijn,^a Tom J. Savenije,^b Marc C. A. Stuart^c and Jan H. van Esch*^a

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Newly developed conjugated terthiophene surfactants are able to aggregate in water and to act as a host for hydrophobic chromophores, creating a multiple donor-acceptor energy transfer (ET) system by self-assembly.

The transfer of excitation energy in the light harvesting complexes of the photosynthetic system is one of the most important physical processes for life.¹ In the light harvesting complexes multiple donor molecules like chlorophyll absorb light and transfer the excitation energy to a central acceptor molecule where it is further processed to form a charge separated state.² Over the past decade a variety of interesting model systems have been designed and studied to mimic the natural light harvesting antenna system and gain insight into the underlying physical principles.^{3–7} For instance, dendrimers consisting of several donors covalently attached to a central acceptor core have been found to display the antennae effect³ which is one of the key features that make natural light harvesting systems so successful. Even though this covalent strategy has produced a number of interesting systems^{4,5} changing the donors and/or acceptor in such covalent systems remains cumbersome.

The self-assembly of donors and acceptors is an attractive alternative to covalent approaches because of its versatility and flexibility, and moreover, also the natural light harvesting systems are formed completely by self-assembly. Several examples of self-assembled multiple donor–acceptor systems have been reported,^{6,7} however, these systems are either still based on covalently connected donors or display an antenna effect only in some cases.⁸ Therefore, the challenge remains to create light harvesting antenna systems that are completely formed through self-assembly of multiple donors and an acceptor in water.

In our pursuit to develop water-soluble conjugated oligomers, we discovered a fully self-assembling antenna-ETsystem. Here we report on amphiphilic conjugated thiophenes which in water self-assemble into micelles, and can be turned into an ET-system by incorporation of suitable hydrophobic acceptor molecules into the hydrophobic micellar interior. A variety of hydrophobic acceptor molecules can be hosted in the hydrophobic micellar core, leading to stable watersoluble self-assembled ET-systems solely composed of donor and acceptor molecules (Fig. 1). In the case of Nile Red as an acceptor, the system displays an antenna effect and overall a very efficient ET within the assemblies.

Amphiphilic polythiophenes reported before are based on an alternating sequence of hydrophilic and hydrophobic substituted thiophenes, leading to lamellar structures at the air/water interface and in Langmuir–Blodgett multilayers.⁹ It was expected that shorter oligo-thiophenes form more dynamic and small water-soluble aggregates. We synthesized a conjugated (1) and cross-conjugated (2) amphiphilic terthiophene by step-wise Stille couplings of two thiophenes with hydrophilic tetraethylene glycol tails to the central thiophene bearing a hydrophobic hexadecane chain. By slight variation of the structures, we anticipate to vary the type of aggregate as well as the spectroscopic properties. Amphiphilic thiophenes 1 and 2 have been obtained by a multistep synthetic procedure in good yields, and have been fully characterized (see ESI \ddagger).

Terthiophenes 1 and 2 are soluble in water up to concentrations of at least 50 mM to give transparent yellow solutions. Turbidity measurements revealed that the surfactants have cloud points of 23 ± 1 °C and 38 ± 2 °C for compounds 1 and 2, respectively, which are typical for non-ionic oligoethylene



Fig. 1 Schematic representation of the ET-system that is formed from the donor (D) thiophene amphiphiles (1 and 2) and the hydrophobic acceptor (A).

^a Self Assembling Systems, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands. E-mail: j.h.vanesch@tudelft.nl; Tel: +31 15 2782682

^b Opto-electronic materials, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

^c Electron microscopy, Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh, 4, 9747 AG Groningen, The Netherlands

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based surfactants.¹⁰ Surface tension measurements confirmed their amphiphilic character, and the critical micelle concentrations (CMC) for isomers **1** and **2** were reached at 1.0 ± 0.1 mM for both. The surface tension plots show for both **1** and **2** a pretransition at 0.1 mM, however, no changes in absorbance or fluorescence spectra occur around this concentration (*vide infra*). Most likely, this pretransition is due to the formation of premicellar aggregates of **1** and **2**, pointing to a less cooperative association process. Dynamic light scattering confirmed the formation of micellar aggregates above 1.0 mM (20 °C) with diameters of 6 ± 2 nm for **1** and 21 ± 5 nm for **2**. Cryo transmission electron microscopy experiments indicated the formation of spherical micellar and cylindrical micellar morphologies formed by **1** and **2**, respectively.

The terthiophene isomers described here have spectroscopic properties similar to most other terthiophenes.¹¹ The thiophene amphiphiles have absorption maxima at 350 and 330 nm, and emission maxima at 455 nm and 470 nm for 1 and 2, respectively. For these and similar compounds it is known that aggregation can affect the electronic properties of chromophores due to electronic coupling between transition dipole moments.¹² The absorption and emission maxima of thiophene amphiphiles 1 and 2 do not shift and the intensities increase linearly with the concentration up to 1.0 mM. However, above 1.0 mM the absorption spectra of isomer 1 do not follow the Lambert-Beer law, whereas the emission intensities of both 1 and 2 deviate from linearity with increasing concentration, indicating that self-assembly occurs. The above data agree with the formation of micellar aggregates of 1 and 2 in which there is a small electronic coupling between the terthiophene groups at concentrations above 1.0 mM, whereas the pretransition at 0.1 mM should be ascribed to the formation of small pre-micellar aggregates with no significant electronic interactions between the chromophores. The optical properties of the micelles are summarized in Table 1. Observed lifetimes, and quantum yields are close to previously published data on terthiophene analogues.¹³

Micelles of 1 and 2 are in fact aqueous assemblies of multiple chromophores, and therefore they are of potential interest for the construction of self-assembled ET- and antenna systems. A straightforward approach towards such systems would be co-assembly with an acceptor molecule by

 Table 1
 Photophysical properties of thiophenes and mixtures in water

Donor (D)	$\tau_{\rm D}/ps^b$	${\phi_{ m F}}^c$	$k_{\rm F}/10^9~{\rm s}^{-1}$	$k_{\rm NR}/10^9 {\rm ~s}^{-3}$
Isomer 1 Isomer 2	95 125	0.10 0.07	1.1 0.56	9.5 7.4
D/A mix (20	: 1)	$\chi(I_{\rm DA}/I_{\rm D})$	$k_{\rm ET}/10^{10}$	$\sigma^{-1a} \qquad \varphi_{\rm ET}$
1 + Nile Red 1 + TPP		0.25 0.34	3.2 2.0	0.75
2 + INIIe Red 2 + TPP		0.39	1.3 8.9	0.61

^{*a*} k_{ET} was determined using $1/(\chi \tau_{D}) - 1/(\tau_{D})$ where χ is the ratio in emission of D/A (1 mM : 50 μM) and D (λ_{ex} : 350 nm and λ_{em} : 455 nm for isomer 1; λ_{ex} : 330 nm and λ_{em} : 480 nm for isomer 2). ^{*b*} Lifetimes τ_{D} were measured (λ_{ex} : 407 nm) (see ESI, SI11). ^{*c*} The quantum yield (φ_{F}) was determined by using 9,10-diphenylanthracene as a reference.

entrapment of the acceptor in the hydrophobic core. Suitable hydrophobic acceptor molecules are for instance tetraphenylporphyrin (TPP) and Nile Red, because their absorption spectra (λ_{max} (TPP) = 421 nm, and λ_{max} (Nile Red) = 550 nm) nicely overlap with the emission spectra of 1 and 2 (Fig. 2; ESI, SI9[‡]). Nile Red is a well-known fluorescence probe for hydrophobic micro-environments.¹⁴ Addition of Nile Red to an aqueous solution of 1 or 2 leads to a pronounced blue shift and an increase in the intensity of the Nile Red emission. The emission maxima of Nile Red above the CMC of 1 and 2 are comparable to the emission found when Nile Red is solubilized in tert-butanol, indicating the formation of hydrophobic domains in micelles of 1 and 2 in which Nile Red resides. The dependency of the Nile Red emission on the concentrations of 1 and 2 again showed two transitions (ESI, SI4, SI7[‡]). One transition occurs at a high concentration of 1.0 mM for 1 and 2 which is in excellent agreement with the CMC. The other transition is observed at a markedly lower concentration of approximately 0.01 mM for both 1 and 2. Most likely, this transition is due to the formation of premicellar aggregates which can be initiated by hydrophobic probes like Nile Red. Also, the otherwise water-insoluble TPP can be solubilized in water by 1 or 2 above the CMC up to a molar ratio of 1 : 4 (TPP : 1 or 2).



Fig. 2 Normalized abs. (solid) and em. (dashed) of isomer 1 (black) $(\lambda_{max} = \lambda_{exc}; 350 \text{ nm}, \lambda_{em}; 455 \text{ nm})$ in water and TPP (grey) $(\lambda_{max}; 421 \text{ nm}, \lambda_{em}; 655 \text{ nm})$ in THF, depicting the overlap integral (A); normalized abs. (solid) and em. (dashed) of isomer 1 (black) $(\lambda_{max} = \lambda_{exc}; 350 \text{ nm}, \lambda_{em}; 455 \text{ nm})$ in water and Nile Red (grey) $(\lambda_{max}; 550 \text{ nm}, \lambda_{em}; 632 \text{ nm})$ in EtOH, depicting the overlap integral (B); normalized em. of micellar solutions of isomer 1 (solid black) (1.0 mM), $(\lambda_{em}; 455 \text{ nm})$ without and with 50 μ M acceptor (Nile Red (dashed black), λ_{em} ; 618 nm; TPP (dashed grey), λ_{em} ; 655 nm) (C).

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Apparently, TPP can efficiently be accommodated by isomers 1 and 2 in their hydrophobic micro-environments, which directly place donor and acceptor in close proximity.

It was found that when 1 or 2 were combined with the hydrophobic chromophores as acceptors an ET-system in water could be formed, based solely on self-assembly of donors and acceptor due to hydrophobic interactions. To 1.0 mM solutions of amphiphilic thiophenes 1 or 2, different quantities of TPP or Nile Red were added to give acceptor concentrations of 0 to 250 µM. It was observed that the emissions of 1 and 2 are increasingly quenched by the addition of increasing amounts of TPP as indicated by χ (see Table 1), until a plateau is reached at a molar ratio of 1 or 2 to TPP of about 20 : 1 (ESI, SI6, SI10[‡]). The quantum efficiencies are 66% and 92% for combinations 1/TTP and 2/TPP, respectively. Simultaneously an increase in the emission intensity of TPP is observed. These results indicate that there is efficient ET from the thiophenes to the porphyrin. The large overlap of the excitation spectrum with the absorption spectra of the thiophenes, and the similarity of the TPP emission maxima by direct excitation of TPP or via the thiophenes, confirm this conclusion and exclude the formation of excimers and ground state interaction of 1 or 2 with TPP.

Similar observations were made upon the incorporation of Nile Red in micelles of 1 or 2, concluding that also the Nile Red/thiophene combinations display efficient ET. Also, the emission intensity of Nile Red by ET is 20 and 12 times higher by excitation of 1 and 2, respectively, than when Nile Red is directly excited at 550 nm under the same conditions (ESI SI6/10[‡]). Apparently, the micellar assembly acts as a light absorbing antenna in which the presence of multiple thiophene donors increases the absorption cross section and therefore this increase is seen.

When considering the absorption of TPP in the micelles, a 7 nm red shift is observed for the absorption while for TTP normally a blue shift is observed with decreasing polarity, which indicates that there is a small coupling between donor and acceptor. A similar interaction is seen in the combination with Nile Red, the emission maximum shifts to the red (~20 nm) and that of the thiophene shifts to the blue (~5 nm). This may be due to a groundstate coupling between donor and acceptor. We suppose that the ET goes *via* the Förster mechanism considering that $k_{\rm ET} > k_{\rm NR}$.

In conclusion, we successfully developed conjugated terthiophene surfactants that aggregate into micellar type assemblies at low concentrations. These micelles can act as a host for hydrophobic chromophores, in which efficient ET can take place between the donor aggregate and the acceptor. This approach gives access to new antenna systems which are completely formed by self-assembly of small molecular components and can easily be modified by varying the hydrophobic acceptor.

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