

Chromophores

Synthesis and Photophysical Properties of Multichromophoric Carbonyl-Bridged Triarylamines

Andreas T. Haedler,^[a] Sebastian R. Beyer,^[b] Natalie Hammer,^[c] Richard Hildner,^{*[b]} Milan Kivala,^{*[c]} Jürgen Köhler,^[b] and Hans-Werner Schmidt^{*[a]}





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Abstract: The synthesis and photophysical properties of two novel multichromophoric compounds is presented. Their molecular design comprises a carbonyl-bridged triarylamine core and either naphthalimides or 4-(5-hexyl-2,2'-bithiophene)naphthalimides as second chromophore in the periphery. The lateral chromophores are attached to the core via an amide linkage and a short alkyl spacer. The synthetic approach demonstrates a straightforward functionalization strategy for carbonyl-bridged triarylamines. Steady-state and

Introduction

Exploiting the unique properties of organic matter for electronic applications holds great promise. Not only does the production of organic materials and devices typically need less resources and energy than their inorganic counterparts, but organic materials also have the potential to open up new applications in light harvesting and solar energy conversion. In particular, functional π -conjugated systems are of key interest for such applications, because they possess appealing optoelectronic properties.^[1] However, an order of magnitude estimate, based on the absorption cross-section of a typical organic chromophore and the number of photons provided from the sun, yields that under optimum conditions an organic molecule would absorb only a few photons per second. $\ensuremath{^{[2]}}$ From this it becomes clear that employing organic matter for any kind of solar energy conversion requires an efficient light-harvesting apparatus (an antenna) for collecting as many photons as possible. This requirement is nicely illustrated by the setup of the natural light-harvesting machineries where hundreds of lightabsorbing chromophores, organized in protein complexes serve for the collection of sunlight, whose energy is transferred efficiently among these chromophores to a special pair of pigments, which initiates an electron transfer chain thereby acting as a transducer.^[3] The attempt to mimic these biological systems led to a number of different approaches aiming for an

[a] A. T. Haedler,⁺ Prof. H.-W. Schmidt Macromolecular Chemistry I, Bayreuther Institut für Makromolekülforschung (BIMF) and Bavreuther Zentrum für Kolloide und Grenzflächen (BZKG) University of Bayreuth, 95440 Bayreuth (Germany) Fax: (+49) 921-55-3206 E-mail: hans-werner.schmidt@uni-bayreuth.de [b] S. R. Beyer,⁺ Dr. R. Hildner, Prof. Dr. J. Köhler Experimental Physics IV and Bayreuther Institut für Makromolekülforschung (BIMF) University of Bayreuth, 95440 Bayreuth (Germany) Fax: (+49) 921-55-4002 E-mail: richard.hildner@uni-bayreuth.de [c] N. Hammer, Dr. M. Kivala Chair of Organic Chemistry I, Department of Chemistry and Pharmacy University of Erlangen-Nürnberg, 91054 Erlangen (Germany) Fax: (+49) 9131-85-23429 E-mail: milan.kivala@fau.de [⁺] Both authors contributed equally. Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403667.

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time-resolved spectroscopic investigations of these compounds, in combination with three reference compounds, provide clear evidence for energy transfer in both multichromophoric compounds. The direction of the energy transfer depends on the lateral chromophore used. Furthermore, the compound bearing the lateral 4-(bithiophene)naphthaimides is capable of forming fluorescent gels at very low concentrations in the sub-millimolar regime whilst retaining its energy transfer properties.

excess of donor chromophores, which funnel the excitation energy into a small number of acceptor chromophores. Despite extensive research the structural diversity of the employed chromophoric systems remains rather narrow and comprises mostly rylene diimides,^[4] fullerenes,^[5] porphyrins, and phthalocyanines,^[6] potentially decorated with thiophene and triarylamine donors.^[7] Furthermore, multichromophoric dendritic,^[8] polymeric,^[9] and supramolecular systems^[10] were investigated.

Promising alternative building blocks are bridged C₃-symmetric triarylamines, so-called heterotriangulenes,^[11] in particular with three electron-withdrawing carbonyl moieties. When suitably substituted, these compounds form columnar structures^[12] and possess tuneable photophysical properties.^[13,14] The carbonyl-bridged triarylamine (CBT) moiety acts as a moderate electron acceptor with appealing optoelectronic and materials characteristics for organic electronics applications.^[15] For example, star-shaped CBT-derivatives, bearing directly connected lateral carbazole moieties, have been reported as electroluminescent materials in organic light emitting diodes.^[16]

Synthetic procedures to obtain functionalized carbonylbridged triarylamines as well as basic studies of their photophysical properties are still rare. Herein, we present two threearmed multichromophoric compounds 1 and 2 comprising the carbonyl-bridged triarylamine core with either three naphthaimide (NI) or three 4-(5-hexyl-2,2'-bithiophene)naphthalimide (NIBT) chromophores in the periphery (Figure 1). The bridged triarylamine and the chromophores in the periphery are linked by an amide unit and a short alkyl spacer to break the conjugation between the chromophores. To understand the photophysical properties of the multichromphoric compounds 1 and 2, three reference compounds 3-5 (Figure 2) were synthesized. In the following, we demonstrate that the energy transfer in 1 proceeds from the naphthalimide periphery to the CBT core and in 2 from the core to the 4-(5-hexyl-2,2-bithiophene)naphthalimide.

Results and Discussion

Synthesis

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The synthetic routes towards the multichromophoric compounds **1** and **2** are shown in Scheme 1. Starting from 1,8naphthalic anhydride **6** via the carboxylic acid **7**, the first pe-





Figure 1. Molecular structures of the multichromophoric compounds 1 and 2 comprising a carbonyl-bridged triarylamine (CBT, highlighted in green) with peripheral naphthalimides (NI, left) and 4-(5-hexyl-2,2'-bithiophene)naphthalimide (NIBT, right) chromophores.



Figure 2. Chemical structures of the reference compounds **3–5** representing the CBT core, the naphthalimide (NI), and the 4-(5-hexyl-2,2'-bithiophene)-naphthalimide (NIBT) moiety, respectively.

ripheral building block **8**, bearing the naphthalimide (NI), was readily accessible in two steps.^[17] The second peripheral building block **13**, containing the 4-(5-hexyl-2,2'-bithiophene)naphthalimide (NIBT) chromophore, was obtained by reacting 4-chloro-1,8-naphthalic anhydride **9** with 4-aminobutyric acid introducing the aliphatic spacer. To prevent substitution of the

chlorine of the naphthalimide **9** by the amino group of the 4aminobutyric acid, ethanol was used instead of *N*,*N*'-dimethylformamide as solvent. Furthermore, the carboxylic acid group was converted into the corresponding ethyl ester **10** in a twostep–one-pot reaction. We applied a Pd-catalyzed arylation to directly couple 5-hexyl-2,2'-bithiophene to the chlorinated naphthalimide to obtain **11** with 80% yield. After basic hydrolysis of the ethyl ester group, the carboxylic acid **12** was converted with oxalylchloride into the corresponding acid chloride **13**. 2,6,10-triamino-CBT **15** was obtained by Pd-catalyzed hydrogenation of 2,6,10-trinitro-CBT **14**, which was synthesized from methyl 2-aminobenzoate and methyl 2-iodobenzoate following reported procedures.^[13, 18] Reaction of 2,6,10-triamino-CBT core **15** with acid chlorides allows for the preparation of a great variety of different CBT derivatives.

From the CBT core **15** and the two peripheral building blocks **8** and **13** we obtained the multichromophoric molecules **1** and **2**. Both compounds were clearly identified by analytical techniques such as ¹H NMR, ¹³C NMR, and ¹H–¹H-COSY (Supporting Information, Figures S1 and S2), FTIR spectroscopy, and matrix-assisted laser desorption ionization with time of flight detection mass spectrometry (MALDI-TOF MS).

The reference compound **3** was synthesized by conversion of nonanoyl chloride with the 2,6,10-triamino-CBT core **15**. The aliphatic substituent was chosen to provide sufficient solubility in common organic solvents. For the reference compounds **4** and **5**, aniline was reacted with the intermediates **8** and **13**, respectively.

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Scheme 1. Overview of the synthetic steps to the multichromophoric compounds 1 and 2. NMP = N-methyl-2-pyrrolidone, DMF = N,N-dimethylformamide.

Photophysical and electronic characterization

The photophysical properties of the two multichromophoric compounds 1 and 2 were investigated in solution by UV/Vis absorption, steady-state, and time-resolved photoluminescence (PL) spectroscopy. To facilitate the interpretation of the data, we also studied the reference compounds 3-5 with molecular structures as close as possible to their respective π -conjugated subunits in the multichromophoric systems. Furthermore, the photoluminescence quantum yields (PL-QY) were determined for all five compounds using an integrating sphere. For all of the measurements, 1,1,2,2-tetrachloroethane (TCE) was used as it is a good solvent for these compounds. The concentration of the CBT derivatives 1-3 was adjusted to 1 μm, while for the naphthalimide and the 4-bithiophenenaphthalimide bearing reference compounds 4 and 5 the concentration was set to 3 µм, to account for the three-armed geometry of compounds 1 and 2. Photoluminescence emission maps of all five compounds were recorded varying the excitation wavelength between 280 and 700 nm (Supporting Information, Figure S3). Two additional maps were recorded from mixed solutions of compounds 3+4 and 3+5 for comparison with the multichromophoric systems 1 and 2. From these maps, PL emission and PL excitation spectra could be extracted for different excitation and emission wavelengths. The time-resolved spectra

were recorded on custom-build streak camera setups with picosecond time-resolution using excitation wavelengths of either 360 nm for compounds **1** and **4** or 440 nm for compounds **2**, **3**, and **5** (see the Experimental Section for more details). The relevant photophysical properties are summarized in Table 1.

Reference compounds

We start the discussion with the CBT reference compound **3**. The absorption spectrum shows two distinct peaks (Figure 3, solid line): an aromatic π - π * transition at 278 nm with a shoulder at 300 nm and a weak bathochromically shifted absorption at 459 nm. An illustrative PL spectrum of compound **3** upon excitation of the lowest-energy absorption peak at 440 nm is shown in Figure 3 (dashed line), which was picked from the respective photoluminescence emission map (Supporting Information, Figure S3 A). A single fluorescence band is observed at 490 nm with a small vibronic shoulder at around 520 nm. The PL emission map reveals that the emission maximum is independent of the excitation at 440 nm, shows a clear monoexponential behavior with a time constant of τ = 2.5 ns (Supporting Information, Figure S4) and the photolumi

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Table 1. Optical and electronic data of compounds 1–5.								
	λ _{max} ^[a] [Abs.	nm] PL	PL-QY ^[b] [%]	τ ^[c] [ns]	LUMO ^[d] [eV]	Opt. gap ^[e] [eV]		
1	281 340 460	492	ca. 10	0.307(r) 3.6	_	2.5		
2	279 340 433	608	ca. 10	0.041 2.4	-	2.3		
3	278 459	489	ca. 15	2.5	-3.22	2.5		
4 5	338 335	382 609	ca. 5 ca. 25	0.495 0.017	-3.06 -3.22	3.4 2.3		
5	335 433	609	ca. 25	0.017 2.5	-3.22	2.3		

[a] Measured in TCE solution, $c = 1-3 \mu M$. [b] Photoluminescence quantum yield (PL-QY), averaged over 4 measurements. The excitation wavelength was 340 nm for compounds 1 and 4 and 440 nm for compounds 2, 3, and 5. [c] PL lifetime. Multiple values mark multiexponential behavior, **r** denotes rising component. [d] Determined by cyclic voltammetry in NMP with respect to ferrocene. [e] Determined from the absorption onset in UV/Vis measurements.



Figure 3. Absorbance (——) and PL emission (•••••) spectrum of compound **3** at $c = 1 \ \mu m$ in 1,1,2,2-tetrachloroethane (TCE). PL was excited at $\lambda_{exc} = 440 \ nm$.

nescence quantum yield (PL-QY) of the CBT reference compound was determined to be about 15%.

The absorption spectrum of the second reference compound **4** comprising the naphthalimide exhibits a vibronically structured $S_0 \rightarrow S_1$ transition peaking at 338 nm (Figure 4, solid line), which is typical for these chromophores. The photolumi-



Figure 4. Absorbance (——) and PL emission (•••••) spectrum of compound **4** at $c = 3 \mu \mu$ in 1,1,2,2-tetrachloroethane (TCE). PL was excited at $\lambda_{exc} = 340 \text{ nm}.$

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nescence spectrum upon excitation at 340 nm (Figure 4, dashed line) reveals the expected vibronically structured naphthalimide fluorescence peaking at around 382 nm,^[19] which is independent of the excitation wavelength as shown in the PL emission map (Supporting Information, Figure S3 B). The timeresolved PL decay features a monoexponential behavior with a time constant of $\tau = 495$ ps (Supporting Information, Figure S5), and the PL QY was determined to be about 5%.

The last reference compound **5** bearing the 4-bithiophenenapthalimide shows absorption over a broad range from 280 to almost 550 nm with two main peaks (Figure 5, solid line). A



Figure 5. Absorbance (——) and PL emission (·····) spectrum of compound **5** at $c=3 \mu m$ in 1,1,2,2-tetrachloroethane (TCE). PL was excited at $\lambda_{exc} = 440 \text{ nm}.$

higher-energy peak is located at 335 nm and a broad and unstructured peak can be detected around 440 nm, which we attribute to a charge-transfer (CT) absorption between the covalently linked electron-deficient naphthalimide and the electronrich bithiophene. This CT character is reflected in the broad and unstructured photoluminescence between 500 and 800 nm peaking at 609 nm (Figure 5, dashed line), independent of the excitation wavelength (Supporting Information, Figure S3C). The PL transient of this compound exhibits a more complex multiexponential decay that can best be described by two exponents with time constants of $\tau_1 = 17 \text{ ps}$ and $\tau_2 =$ 2.5 ns and an amplitude ratio of $A_1A_2^{-1} = 1.57$ (Supporting Information, Figure S6). Compound 5 possesses the highest PL-QY (ca. 25%) of the reference compounds, which is in accordance with the strong emission intensity of the illustrative spectrum shown in Figure 5.

From the spectra of the reference compounds **3–5** shown in Figures 3–5 and in the Supporting Information, Figures S3 A–C, it is clear that the spectral shape of the photoluminescence of these substances is independent of the excitation wavelength. The peak maximum of the PL can be easily attributed to the naphthalimides (382 nm), the carbonyl-bridged triarylamine (489 nm), and the 4-bithiophenenaphthalimide (609 nm). The characterization of the individual chromophores shows a significant spectral overlap between the PL of the naphthalimide (NI) and the absorption of the carbonyl-bridged triarylamine (CBT) as well as between the PL of the CBT and the absorption of the 4-bithiophenenaphthalimide (NIBT). This is an important prerequisite for efficient energy transfer.



For a detailed characterization of organic molecules not only the photophysical but also the electronic properties are of interest. Therefore, we performed cyclic voltammetry (CV) measurements using the reference compounds 3-5 in N-methyl-2pyrrolidone (NMP). The three compounds representing the individual chromophores show reversible reductive peaks (Supporting Information, Figures S8-10), while meaningful oxidation potentials could not be determined owing to inhibition of the electrode. Comparison of the reductive waves with a ferrocene standard revealed LUMO (lowest unoccupied molecular $orbital)^{\mbox{\tiny [20]}} \mbox{ levels of the carbonyl-bridged triarylamine derivative}$ 3 and the 4-bithiophenenaphthalimide 5 to be identical at -3.22 eV, while the naphthalimide **4** exhibits a slightly higher value of -3.06 eV (Table 1). The optical gaps are 3.4 eV for compound 4, 2.5 eV for compound 3, and 2.3 eV for compound 5 (Table 1; Supporting Information, Figures S8–S10).

Multichromophoric compounds

Having characterized the reference compounds, we now turn to the photophysical properties of the more complex multichromophoric systems **1** and **2**. In both compounds the CBT core is in close proximity of a few nanometers to the respective peripheral chromophore, which should facilitate energy transfer. The UV/Vis absorption spectra of both multichromophoric systems are a superposition of the absorption of their respective chromophoric parts with only slight differences in the shape of the bands and in the position of their maxima (Figure 6A and Figure 7A, solid lines). For both compounds **1** and **2**, neither strongly shifted nor additional absorption peaks are observed with respect to the reference materials, which indicates that the electronic coupling between the subunits is weak.

The PL response of compound 1 shows the characteristic emission signature of the CBT core upon excitation at 340 nm but no photoluminescence from the peripheral naphthalimide (Figure 6A, dashed line). This behavior is independent of the excitation wavelength (Supporting Information, Figure S3F) throughout the whole absorption regime of compound 1. From the PL emission map, we also extracted the PL excitation spectra of compound 1 for detection wavelengths that represent the characteristic PL signature of the naphthalimide (372-392 nm) and the CBT core (480-500 nm). The PL excitation spectrum that was detected in the spectral emission window of the CBT core (Figure 6A, green box) follows the absorption spectrum of compound 1 closely without major deviations. Thus, it incorporates the absorptive channels of the CBT core as well as those of the peripheral NI. The PL excitation spectrum that was detected in the spectral emission window of the peripheral NI, on the other hand, shows no signal at all (Figure 6A, blue box). This means that both the absorption of the CBT core and of the peripheral naphthalimides result in PL of the CBT core. In a control experiment with a mixed solution of reference compounds 3 and 4 (Supporting Information, Figure S3D), the chromophores are on average about 75 nm apart, which renders energy transfer highly unlikely. In this experiment, photoluminescence stems either from the carbonyl-





Figure 6. Photophysical properties of compound 1 in 1,1,2,2-tetrachloroethane (TCE) at $c = 1 \ \mu$ m. A) Absorbance (black ——) and PL emission spectrum at $\lambda_{exc} = 340 \ nm$ (·····). The features observed in the PL emission spectrum between 370 and 450 nm are of instrumental origin and appear in all of the spectra at such low intensities. PL excitation spectra detected at the spectral emission window of the NI periphery (blue line, detected 372– 392 nm) and the CBT core (green line, detected 480–500 nm). B) Time-resolved PL emission at $\lambda_{exc} = 360 \ nm$ (——). The instrument response function (IRF, ·····) was measured with scattered excitation light. Fitting resulted in a multiexponential decay with $\tau_{decay} = 3.6 \ ns$ and $\tau_{rise} = 307 \ ps$.



Figure 7. Photophysical properties of compound **2** in 1,1,2,2-tetrachloroethane (TCE) at $c = 1 \ \mu$ m. A) Absorbance (black —) and PL emission spectrum at $\lambda_{exc} = 440 \ nm$ (·····). PL excitation spectra detected at the spectral emission window of the NIBT periphery (orange line, detected 600–620 nm) and the CBT core (green line, detected 480–500 nm). B) Time-resolved PL emission at $\lambda_{exc} = 440 \ nm$ (—). The instrument response function (IRF, ·····) was measured with scattered excitation light. Fitting resulted in a biexponential decay with $\tau_1 = 41 \ ps$, $\tau_2 = 2.4 \ ns$, and $A_1A_2^{-1} = 1.55$.

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bridged triarylamine or from the naphthalimide chromophore, depending on which chromophore is addressed at the particular excitation wavelength. These findings suggest that in compound 1, the energy absorbed by the peripheral naphthalimide (energy donor) is funneled to the carbonyl-bridged triarylamine core (energy acceptor) by intramolecular energy transfer.

Time-resolved PL measurements provide direct evidence for energy transfer. For these experiments on compound 1, we excited at 360 nm where the absorption of the naphthalimide is prominent while that of the core is negligible, and integrated the PL spectrally from 450 to 580 nm. The resulting PL decay curve (Figure 6B, solid line) features a clear rising component with a time constant of 307 ps followed by a monoexponential decay with a time constant of 3.6 ns. As we almost exclusively excite the NI periphery, the rising component in the PL transient from the CBT core clearly demonstrates energy transfer from the periphery to the core. We note that the time constant of the decay of compound 1 is longer with respect to reference compound 3. Presumably, this reflects a change in the dielectric environment owing to the different molecular structure. The quantum yield of the energy transfer can be estimated according to a standard kinetic model (Supporting Information, pages S6-S7). The obtained rise time corresponds to the inverse sum of the rates that depopulate the NI exited state $\tau_{\rm rise} = (\Gamma + k_{\rm nr} + k_{\rm trans})^{-1}$ with Γ being the radiative and $k_{\rm nr}$ the nonradiative rate of NI and k_{trans} the transfer rate from NI to CBT. Assuming that for the NI chromophore in reference compound **4** and in compound **1**, Γ and k_{nr} remain constant, we can estimate the energy transfer time to be $(k_{\text{trans}})^{-1} = 808 \text{ ps}$ and the energy transfer quantum yield from NI to CBT to be $k_{\text{trans}}/(k_{\text{trans}}+\Gamma+k_{\text{nr}})=0.38$, with $(\Gamma+k_{\text{nr}})^{-1}=495$ ps being the observed lifetime of NI in compound 4.

Compound 2 shows the characteristic PL signature of the peripheral 4-bithiophenenaphthalimide at around 610 nm when excited at 440 nm (Figure 7 A, dashed line). Yet, the spectral signature of the CBT core around 492 nm cannot be observed. The PL emission map (Supporting Information, Figure S3G) shows that this holds true for all employed excitation wavelengths from 280 to 600 nm. As the peripheral NIBT chromophore absorbs over a broad spectral range, it is not possible to exclusively excite the carbonyl-bridged triarylamine. However, the PL excitation spectrum detected in the emission range of the NIBT (600-620 nm, Figure 7 A orange box) reproduces the absorption spectrum of compound 2 very well. In contrast, the respective spectrum detected in the PL range of the CBT core (480-500 nm; Figure 7B green box) shows no signal at all. Therefore, it can be concluded that the absorption of both chromophores contribute to the emission of the NIBT. Furthermore, in a control experiment on a mixed solution of compounds **3** and **5** (Supporting Information, Figure S3E), where energy transfer can be excluded, an additional PL peak arises at around 500 nm that can be clearly assigned to the central carbonyl-bridged triarylamine, after excitation in the absorption regime of that chromophore. This peak is not present in the spectra of the multichromophoric compound 2. These results provide first evidence for an intramolecular energy transfer in compound **2** from the triarylamine core to the peripheral chromophores.

The time-resolved PL transient for compound 2 was recorded upon excitation at 440 nm and spectrally integrated from 480-600 nm, according to the procedure employed for compound 1. Interpretation of the time-resolved photoluminescence spectrum of compound 2 (Figure 7B, solid line) is, however, more challenging. Just like for compound 5, we find a biexponential transient with decay times of $\tau_1 = 41$ ps and $\tau_2 = 2.4$ ns with an amplitude ratio of $A_1 A_2^{-1} = 1.55$. Within the experimental uncertainty, the values for compounds 2 and 5 are identical. We could not identify a rising component in the transient of 2. This is due to two factors: 1) the core distributes its energy to three peripheral molecules, which results in a shortening of the rise time; and 2) we simultaneously excite the core and the periphery, where the latter possesses a much larger absorption cross-section. This is in agreement with a kinetic model (Supporting Information, pages S6-S7) that predicts a 2- to 6-fold decrease in the amplitude of the rising component of the acceptor chromophore relative to the amplitude of the decay of the donor. Therefore, we cannot determine the efficiency for the transfer from CBT to NIBT in compound 2. Yet, from steady state spectroscopy, we have evidence that this transfer occurs.

A PL-QY of 10% was found for both mutlichromophoric compounds 1 and 2. This is lower compared to the PL-QYs of the reference compounds 3 and 5 representing the respective acceptor chromophore and can be rationalized with the larger molecular structures of 1 and 2, which enables additional non-radiative relaxation pathways due to structural distortion.

Cyclic voltammetry experiments on compounds 1 and 2 did not yield meaningful results owing to electrode inhibition. However, in the multichromophoric compounds 1 and 2, the constituent chromophores are electronically decoupled by alkyl spacers, which efficiently break the conjugation. Therefore, the positions of the energy levels and thus also the optical gaps are presumably very close to those of the structurally similar reference compounds 3–5. The LUMO values and the optical gaps of the reference compounds 3–5 rationalize the direction of the energy transfer: from the peripheral naphthaimide to the central carbonyl-bridged triarylamine in compound 1 and from the carbonyl-bridged triarylamine to the 4bithiophenenaphthalimide in the periphery of compound 2.

An interesting feature of compound **2** is the formation of transparent fluorescent gels of orange color in *ortho*-dichlorobenzene at very low concentrations down to 0.7 mM (Figure 8A). The PL emission map of a gelled sample reveals that the photophysical properties are very similar in the gel state and in dilute solution (Supporting Information, Figure S11). In particular the emission of the CBT core at around 500 nm is still quenched by energy transfer to the periphery, independent of the excitation wavelength (Figure 8B). To the best of our knowledge, this is the first time that a supramolecular gel is obtained based on a CBT derivative. Detailed investigation of this phenomena and the characterization of the resulting gel is a part of ongoing work.

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Figure 8. A) Photoluminescent gel of compound **2** in *ortho*-dichlorobenzene (*o*-DCB; *c* = 0.7 mm); right: excitation at 366 nm. B) PL emission spectra of the gelled sample upon excitation at λ_{exc} = 340 nm (black line) and 440 nm (orange line). The dashed box marks the spectral area where PL of the CBT core would be expected.

Conclusion

We presented a newly developed reliable synthetic route to functionalize the periphery of carbonyl-bridged triarylamines. The three-armed multichromophoric systems 1 and 2 comprise next to the carbonyl-bridged triarylamine core either naphthalimides or 4-(5-hexyl-2,2'-bithiophene)naphthalimides as peripheral chromophores, respectively. Steady-state and time-resolved spectroscopy of 1 and 2 in comparison with three reference compounds 3-5 provide clear evidence for energy transfer in both multichromophoric compounds. For system 1, the energy is funneled from the peripheral naphthalimides (energy donor) to the carbonyl-bridged triarylamine core (energy acceptor). In the second system (compound 2), the energy transfer proceeds in the opposite direction; that is, from the carbonyl-bridged triarylamine core (energy donor) to the 4-(5hexyl-2,2'-bithiophene)naphthalimides (energy acceptor) in the periphery. Furthermore, the latter compound is an efficient gelator for ortho-dichlorobenzene (0.7 mm) and retains its energy transfer and photoluminescent properties in the gel state.

Experimental Section

Synthetic materials and methods

If not mentioned otherwise, all commercially available starting materials and solvents were used as received. *N*-Methyl-2-pyrrolidone (NMP) was stirred over CaH_2 for 2 days, then fractionally distilled and stored under argon before use. All of the NMR data were recorded on a Bruker Avance 300 spectrometer at 300.1 MHz in deuterated solvents at 298 K. Gas chromatography with mass spectrometry was recorded on a Finnigan MAT 8500 GC/MS. Matrix-as-

sisted laser desorption ionization spectrometry with time of flight mass spectrometry (MALDI-TOF MS) measurements were performed on a Bruker Reflex III in reflection mode using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix and silver trifluoroacetate (AgTFA) as cationizing salt. Solutions of the analyte (1 mg/200 µL), the matrix (1 mg/100 µL), and the cationizing salt (1 mg/100 µL) in chloroform with 1 vol% trifluoroacetic acid were mixed in the ratio 5:20:1 (v:v:v) and spotted onto the MALDI target plate prior to the measurement. The laser intensity was set to around 25%. Thermogravimetric analysis was conducted on a TGA/DTA 851e from Mettler Toledo. Differential scanning calorimetry was conducted on a Diamond DSC from Perkin–Elmer.

UV/Vis absorption spectroscopy

All of the UV/vis spectra were recorded on a PerkinElmer Lambda 750 Spectrophotometer with a scan speed of 274 nm min⁻¹, a spectral resolution of 2.0 nm, and a data interval of 1 nm in the range of 250–1100 nm (for clarity we do not show the full range). The solutions were measured directly after preparation in 10 mm Hellma QS quartz-glass cuvettes at room temperature. As solvent, 1,1,2,2-tetrachloroethane (TCE) was used as received.

Photoluminescence (PL) spectroscopy

All PL spectra were recorded on a JASCO FP-8600 Spectrofluorometer with a scan speed of 200 nm min⁻¹ and a data interval of 0.4 nm from 10 nm above the excitation wavelength to 800 nm. The excitation and emission bandwidth were set to 5 and 2 nm, respectively, with a 0.1 s response time. For the photoluminescence (PL) emission maps (Supporting Information, Figure S4) the excitation wavelength was varied in 2 nm steps from 280 to 700 nm. The solutions were measured directly after preparation in 10 mm Hellma QS quartz-glass cuvettes at room temperature. As solvent, 1,1,2,2-tetrachloroethane (TCE) was used as received. Compounds that contain 4-(5-hexyl-2,2'-)naphthalimide (2 and 5) show strong photo-bleaching upon excitation in the high-energy range of the spectrum. To avoid corruption of the PL emission maps by this effect, we had to replace solutions containing these compounds by unilluminated samples in distinct intervals. The excitation wavelengths at which the sample was replaced are marked by dashed horizontal lines in the Supporting Information, Figure S3.

Time-resolved spectroscopy

Time-resolved measurements were performed with different custom-built setups. The excitation source was always a frequencydoubled, pulse-picked Ti:sapphire laser systems (Tsunami, Spectra Physics or Chameleon 2 Ultra, Coherent). The laser light was focused onto the samples that were held in quartz-glass cuvettes. The emission signal was collected in a right-angle geometry and directed to Streak-camera systems equipped with imaging spectrographs (Hamamatsu C5680 with spectrograph 250IS, Bruker, or Optronis SRU-BA with spectrograph Acton SP2300, Princeton Instruments).

Compounds **2**, **3**, and **5** were excited at 440 nm with a repetition rate of 810 kHz, and a fluence of 10^{13} photons/pulse/cm². The instrument response function for these measurements was 78 ps (FWHM). Compounds **1** and **4** were excited at 360 nm with a repetition rate of 8 MHz and a fluence of 3.6×10^{14} photons/pulse/cm². The FWHM of the instrument response function was 410 ps. As the repetition rates and fluences of the excitation light were kept as low as possible to avoid annihilation processes, we had to spectral-

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ly integrate the emission signal from all of the compounds. For data analysis, we used home-written software to conduct a reconvolutive (multi-) exponential fit, taking into account the instrument response function of the system.

Cyclic voltammetry, LUMO values, and optical gaps

Cyclic voltammetry measurements were conducted on a Pt working electrode with 0.1 $\mbox{Mg/AgNO}_3$ in acetonitrile as reference electrode. We used 0.1 \mbox{M} tetrabutylammonium hexafluorophosphate in distilled NMP as solvent, scanning the range from -2.5 to +0.5 V at 50 mV s⁻¹. Reduction potentials were determined by the half-wave potential of the reversible cathodic peak potential and anionic peak potential. Ferrocene (FC) was used as internal standard to calculate the (approximate) LUMO values of compounds **3**–**5** assuming a HOMO level of ferrocene in NMP at -4.8 eV.^[20] In all cases, at least 10 cycles were conducted to demonstrate the reversibility of the reduction and re-oxidation processes of the compounds. The optical gaps were determined from the UV/Vis absorption onset of the respective chromophore (**3**–**5**) in TCE (Supporting Information, Figures S8–S10).

Synthesis

Synthesis of compounds ${\bf 7}$ and ${\bf 14}$ were performed following literature procedures. $^{[13,17,18]}$

Synthesis of the acid chlorides **8** and **13**: Under an argon atmosphere, the respective acid (1 equiv) was dissolved in dichloromethane (75 mL per 15 mmol acid) in a previously baked roundbottom flask, and a few drops of *N*,*N*-dimethylformamide were added. The mixture was cooled to 0° C before 5 equiv of oxalyl-chloride were added. The reaction mixture was stirred at room temperature for 12 h. After the reaction was finished, the solvent and the remaining oxalylchloride were removed under high vacuum. The precipitated product was stored under argon and used without further purification.

Synthesis of compound 10: In a round-bottom flask with a reflux condenser, 4-chloro-1,8-naphthalic anhydride **9** (26.9 g, 1.0 equiv, 115.7 mmol) and 4-aminobutyric acid (11.9 g, 1.0 equiv, 115.7 mmol) were dissolved in ethanol (750 mL). The mixture was refluxed for 6 h before H_2SO_4 (conc., 5 mL) was added and then further refluxed for 12 h. The reaction mixture was cooled to room temperature and the precipitate was filtered off, washed three times with diethyl ether, and dried. The product was obtained as light yellow powder in 81% yield (32.5 g). ¹H NMR (300.1 MHz, CDCl₃): $\delta = 1.25$ (t, 3H, OCH₂CH₃), 2.11 (quin, 2H, CH₂CH₂CH₂), 2.45 (t, 2H, CH₂CH₂CO), 4.12 (quart, 2H, OCH₂CH₃), 4.26 (t, 2H, NCH₂CH₂), 7.82–7.89 (t, 1H, CHCHCH, d, 1H, CICCH), 8.51 (d, 1H, CICCHCH), 8.61 (d, 1H, CHCHCH), 8.67 ppm (d, 1H, CHCHCH).

Synthesis of compound 11: K_2CO_3 (370 mg, 1.5 equiv, 2.7 mmol) was added in a round-bottom flask equipped with a reflux condenser and baked and dried with the glassware. Under an argon atmosphere, compound **10** (617 mg, 1.0 equiv, 1.8 mmol), 5-hexyl-2,2'-bithiophene (1.1 mL, 1.11 g, 2.5 equiv, 4.5 mmol), Pd(OAc)₂ (8 mg, 0.02 equiv, 0.04 mmol), PCy₃·HBF₄ (26 mg, 0.04 equiv, 0.1 mmol), pivalic acid (55 mg, 0.3 equiv, 0.5 mmol), and toluene (6 mL) were added. The mixture was degased three times before it was refluxed for six days. The reaction mixture was filtered and the solvent was evaporated. The crude product was pre-purified by column chromatography (silica gel, toluene/THF, 15:1). The fractions containing the product were dried and recrystallized from acetone. The product was obtained as orange powder in 80% yield (800 mg). ¹H NMR (300.1 MHz, CDCl₃): δ =0.93 (t, 3 H, CH₂

CH₂CH₃), 1.26 (t, 3 H, OCH₂CH₃), 1.32–1.42 (m, 6 H, CH₂(CH₂)₃CH₂), 1.73 (quin, 2 H, CH₂CH₂CS), 2.14 (quin, 2 H, CH₂CH₂CH₂), 2.45 (t, 2 H, CH₂CH₂CO), 2.85 (t, 2 H, CH₂CS), 4.13 (quart, 2 H, OCH₂CH₃), 4.30 (t, 2 H, NCH₂CH₂), 6.76 (d, 1 H, CH₂CCH), 7.11 (d, 1 H, CH₂CCHCH), 7.24– 7.28 (d, 2 H, CHCHCC-NI), 7.80 (t, 1 H, CHCHCH), 7.85 (d, 1 H, BT-CCH), 8.62 (d, 1 H, BT-CCHCH), 8.67 (d, 1 H, CHCHCH), 8.74 ppm (d, 1 H, CHCHCH).

Synthesis of compound 12: In a round-bottom flask equipped with a reflux condenser, compound 11 (1.19 g, 1.0 equiv, 2.7 mmol) was dissolved in ethanol (15 mL) before a 10 wt% aqueous solution of KOH was added. The mixture was refluxed for 2 h. The reaction mixture was precipitated in aqueous HCl solution, filtered off, washed with water, and dried. The product was obtained as orange powder in 95% yield (1.07 g). ¹H NMR (300.1 MHz, [D₆]DMSO): δ = 0.87 (t, 3H, CH₂ CH₂CH₃), 1.29–1.40 (m, 6H, CH₂-(CH₂)₃CH₂), 1.63 (quin, 2H, CH₂CH₂CS), 1.91 (quin, 2H, CH₂CH₂), 2.32 (t, 2H, CH₂CCH), 2.81 (t, 2H, CH₂CS), 4.11 (t, 2H, NCH₂CH₂), 6.86 (d, 1H, CH₂CCH), 7.25 (d, 1H, CH₂CHCH), 7.41 (d, 1H, CHCHCC-NI), 7.48 (d, 1H, CHCHCC-NI), 7.91–7.95 (t, 1H, CHCHCH, d, 1H, CICCH), 8.49 (d, 1H, BT-CCHCH), 8.55 (d, 1H, CHCHCH), 8.71 (d, 1H, CHCHCH), 12.03 ppm (s, 1H, COOH).

Synthesis of compound 15: In a round-bottom flask equipped with a reflux condenser, compound **14** (335 mg, 1.0 equiv, 0.7 mmol) was dissolved in NMP (25 mL) and cooled to 0 °C. Pd (55 mg) on activated charcoal (25 mg per mmol NO₂) and subsequently hydrazine monohydrate (0.32 mL, 9.0 equiv, 6.6 mmol) was added slowly. The reaction mixture was stirred for 12 h at 100 °C and then cooled to room temperature. The suspension was filtered through silica gel and washed with concentrated H₂SO₄. The solution was then precipitated in an alkaline solution of aqueous NaOH and carefully filtered after the product agglomerated. The product was washed with water, ethanol, and diethyl ether, and finally dried. The product was obtained as deep purple powder in 56% yield (150 mg). ¹H NMR (300.1 MHz, [D₆]DMSO): δ =5.96 (s, 6H, NH₂), 8.09 ppm (s, 6H, CCHC).

General preparation method for the synthesis of the threearmed triangulene trisamides 1–3: The reactions of the triamino compound 15 with the acid chlorides 8, 13, and nonanoyl chloride were conducted under argon and in dry conditions. In a roundbottom flask, compound 15 (1.0 equiv) was dissolved in NMP and the respective acid chloride (5.0 equiv) and pyridine (5.0 equiv) as base were added. The mixture was stirred at 60 °C for 4–5 days and then poured into water. The precipitate was filtered off and washed with water, ethanol, and acetone.

Purification of compound 1: The crude product was recrystallized from DMSO, filtered, and washed with water, ethanol, and acetone. The product was obtained as dark red powder in 40% yield (128 mg). ¹H NMR (300.1 MHz, CDCl₃/[D₁]TFA): δ =2.37 (quin, 6H, CH₂CH₂), 2.85 (t, 6H, CH₂CO), 4.47 (t, 6H, NCH₂CH₂), 7.88 (t, 6H, CHCHCH), 8.38 (d, 6H, CHCHCH), 8.73 (d, 6H, CHCHCH), 9.34 ppm (s, 6H, CCHC); ¹³C NMR (75.5 MHz, CDCl₃/[D₁]TFA): δ =24.1, 34.7, 40.6, 121.1, 123.6, 127.8, 127.9, 128.4, 132.0, 133.5, 134.8, 136.2, 136.7, 167.1, 175.9, 177.9 ppm; IR (neat): \tilde{v} =3258 (m), 3066 (w), 1691 (s), 1647 (s), 1587 (s), 1547 (s), 1464 (s), 1438 (m), 1384 (m), 1342 (s), 1234 (m), 1167 (m), 1141 (m), 1045 (m), 893 (w), 846 (m), 802 cm⁻¹ (s); MALDI-TOF-MS: *m/z* calcd for the Ag adduct C₆₉H₄₅AgN₇O₁₂ [*M*]⁺ 1272.22 gmol⁻¹, found 1272.06 gmol⁻¹; thermally stable up to 300 °C, melting was not observed below decomposition temperature.

Purification of compound 2: The crude product was boiled in *N*,*N*-dimethylformamide for 2 h, cooled, filtered, and washed with water, ethanol, and acetone. The product was obtained as brown powder in 60% yield (300 mg). ¹H NMR (300.1 MHz, $CDCl_3/[D_1]TFA$):

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These are not the final page numbers! **77**



δ = 0.92 (t, 9H, CH₂CH₂CH₃), 1.32–1.43 (m, 18H, CH₂(CH₂)₃CH₂), 1.72 (quin, 6H, CH₂CH₂CS), 2.41 (quin, 6H, CH₂CH₂CH₂), 2.79–2.87 (t, 6H, CH₂CH₂CO, t, 6H, CH₂CS), 4.50 (t, 6H, NCH₂CH₂), 6.75 (d, 3H, CH₂CCH), 7.05 (d, 3H, CH₂CCHCH), 7.15 (d, 3H, CHCHCC-NI), 7.22 (d, 3H, CHCHCC-NI), 7.83–7.89 (t, 3H, CHCHCH, d, 3H, BT-CCH), 8.66 (d, 3H, BT-CCHCH), 8.76 (d, 3H, CHCHCH, 8.80 (d, 3H, CHCHCH), 9.17 ppm (s, 6H, CCHC); ¹³C NMR (75.5 MHz, CDCl₃/[D₁]TFA): δ = 14.0, 22.6, 28.8, 30.2, 31.6, 120.0, 121.0, 122.5, 123.8, 124.4, 125.1, 126.2, 127.6, 128.2, 128.2, 129.2, 130.4, 130.4, 132.1, 133.0, 133.5, 136.1, 136.8, 137.5, 140.4, 141.5, 147.0, 165.5, 165.8, 175.2, 178.3 ppm; IR (neat): v = 3288 (w), 2925 (m), 2853 (m), 1695 (s), 1647 (s), 1585 (s), 1549 (m), 1463 (s), 1384 (m), 1348 (s), 1232 (m), 1156 (m), 1116 (m), 1051 (m), 857 (m), 801 cm⁻¹ (s); MALDI-TOF-MS: *m/z* calcd for the Ag adduct C₁₁₁H₉₃AgN₇O₁₂S₆ [*M*]⁺ 2016.43 g mol⁻¹, found 2016.47 g mol⁻¹.

Purification of compound 3: The crude product was boiled in dimethylformamide for 2 h, cooled, filtered, and washed with water and ethanol. The product was obtained as brown powder in 58% yield (250 mg). ¹H NMR (300.1 MHz, CDCl₃/[D₁]TFA): δ = 0.92 (t, 9H, CH₂ CH₂CH₃), 1.31–1.59 (m, 30H, CH₂(CH₂)₅CH₂), 1.94 (quin, 6H, COCH₂ CH₂), 2.73 (t, 6H, COCH₂), 8.99 ppm (s, 6H, CCHC); ¹³C NMR (75.5 MHz, CDCl₃/[D₁]TFA): δ = 13.8, 22.7, 26.6, 29.2, 29.2, 29.3, 31.9, 37.5, 122.5, 127.1, 132.7, 137.0, 175.8, 178.5 ppm; IR (neat): $\tilde{\nu}$ = 3334 (m), 2921 (s), 2852 (s), 1703 (m), 1660 (m), 1633 (s), 1598 (s), 1548 (s), 1521 (m), 1358 (m), 1285 (m), 1258 (m), 1199 (m), 1158 (m), 1106 (m), 1017 (w), 910 (s), 869 (w), 801 cm⁻¹ (s); MS: *m/z* calcd for C₄₈H₆₀N₄O₆ [*M*]⁺ 788.45 g mol⁻¹, found 788 g mol⁻¹; thermally stable up to 300 °C, melting was not observed below decomposition temperature.

General preparation method for the synthesis of the reference compounds 4 and 5: The reactions of the acid chlorides 8 and 13 with aniline were conducted under argon and in dry conditions. In a round-bottom flask, the respective acid chloride (1.0 equiv) was dissolved in NMP, and aniline (2.5 equiv) was added as reactive amine and as base. The mixture was stirred at 60 °C for 2 days.

Purification of compound 4: The reaction mixture was poured in acidic (HCl) water. The precipitate was filtered off, washed with water, and dried. The crude product was recrystallized from ethanol at 4 °C. The product was obtained as white powder in 79% yield (930 mg). ¹H NMR (300.1 MHz, [D₆]DSMO): δ = 2.30 (quin, 2 H, CH₂CH₂CH₂), 2.72 (t, 2 H, CH₂CH₂CO), 4.40 (t, 2 H, NCH₂CH₂), 7.20–7.39 (m, 5 H, NH-C(CH)₅), 7.84 (t, 2 H, CHCHCH), 8.35 (d, 2 H, CHCHCH), 8.65 ppm (d, 2 H, CHCHCH); ¹³C NMR (75.5 MHz, CDCI₃/ [D₁]TFA): δ = 24.1, 33.9, 40.3, 121.0, 122.2, 127.2, 127.7, 128.2, 129.4, 131.8, 133.3, 135.1, 136.5, 166.8, 175.5 ppm; IR (neat): \tilde{v} = 3279 (s), 3066 (w), 2959 (w), 1696 (s), 1654 (s), 1625 (m), 1590 (s), 1536 (s), 1499 (m), 1438 (s), 1386 (s), 1341 (s), 1246 (s), 1200 (m), 1168 (s), 1142 (m), 1047 (s), 971 (s), 894 (s), 846 cm⁻¹ (s); MS: *m/z* calcd for C₂₂H₁₈N₂O₃ [*M*]⁺ 358.13 gmol⁻¹, found 358 gmol⁻¹; thermally stable up to 300 °C, melting point: 208 °C.

Purification of compound 5: The reaction mixture was poured in acidic (HCl) water. The precipitate was filtered off, washed with water, and dried. The crude product was recrystallized from ethanol at 4°C. The product was obtained as orange powder in 58% yield (290 mg). ¹H NMR (300.1 MHz, [D₆]DSMO): $\delta = 0.87$ (t, 3 H, CH₂ CH₂CH₃), 1.23–1.37 (m, 6H, CH₂(CH₂)₃CH₂), 1.64 (quin, 2H, CH₂CH₂CS), 2.02 (quin, 2H, CH₂CH₂CH₂), 2.40 (t, 2H, CH₂CH₂CO), 2.81 (t, 2H, CH₂CCH*C*), 7.19 (d, 1H, CHCHCC-NI), 7.27 (d, 1H, CHCHCC-NI), 7.46 (m, 5H, NH-C(CH)₅), 7.92 (t, 1H, CHCHCH), 7.94 (d, 1H, BT-CCH), 8.50 (d, 1H, BT-CCHCH), 8.57 ppm (d, 1H, CHCHCH), 8.71 (d, 1H, CHCHCH); ¹³C NMR (75.5 MHz, [D₂]TCE): $\delta =$ 14.2, 22.5, 24.2, 28.7, 30.1, 31.4, 34.9, 39.5, 119.7, 121.0, 122.3,

123.7, 124.1, 124.2, 125.1, 127.3, 128.2, 128.8, 128.9, 129.4, 129.9, 131.0, 131.7, 133.6, 137.3, 138.0, 139.1, 140.5, 146.6, 164.3, 164.6, 170.7 ppm; IR (neat): $\bar{\nu}$ =3289 (m), 3062 (w), 2925 (s), 2854 (m), 1695 (s), 1652 (s), 1585 (s), 1534 (s), 1498 (m), 1438 (s), 1386 (s), 1350 (s), 1311 (w), 1249 (s), 1229 (s), 1174 (m), 1156 (m), 1119 (s), 1055 (s), 965 (m), 897 (s), 865 cm⁻¹ (s); MS: *m/z* calcd for C₃₆H₃₄N₂O₃S₂ [*M*]⁺ 606.20 gmol⁻¹, found 606 gmol⁻¹; thermally stable up to 300°C, melting point: 165°C.

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- [20] It is common practice to associate the potential for formation of the anion (cation) with the energy of the LUMO (HOMO), that is, the oneelectron molecular orbitals of the neutral species. However it is worth to note that LUMO and HOMO are theoretical constructs and their energies cannot be observed by any experimental method. Experimentally accessible is the optical gap which corresponds to the energy difference between the electronic S_0 and S_1 states of the neutral compound.

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FULL PAPER



A. T. Haedler, S. R. Beyer, N. Hammer, R. Hildner,* M. Kivala,* J. Köhler, H.-W. Schmidt*

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Synthesis and Photophysical Properties of Multichromophoric Carbonyl-Bridged Triarylamines



There and back again: Two multichromophoric bridged triarylamines are presented that are functionalized in a straightforward synthetic approach with either three naphthalimides or three 4-(bithiophene)naphthalimides. Efficient energy transfer is observed in both compounds (see figure). In the first case, the energy is funneled from the peripheral naphthalimides, acting as antenna dyes, to the core. In the second, the energy is transferred from the core to the periphery.

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Chromophores

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In their Full Paper on page ff., H.-W. Schmidt, R. Hildnera, M. Kivala et al. describe a reliable synthetic route to functionalize the periphery of carbonyl-bridged triarylamines with either three naphthalimides or three 4-(5hexyl-2,2'-bithiophene)naphthalimides as peripheral chromophores. Steady-state and time-resolved spectroscopy provide clear evidence for energy transfer in both multichromophoric compounds.