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White-Light Emitting Hydrogen-Bonded Supramolecular Copolymers Based on π-Conjugated Oligomers

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Abstract: Three different π-conjugated oligomers (a blue-emitting oligofluorene, a green-emitting oligo(phenylene vinylene), and a red-emitting perylene bisimide) have been functionalized with self-complementary quadruple hydrogen bonding ureidopyrimidinone (UPy) units at both ends. The molecules self-assemble in solution and in the bulk, forming supramolecular polymers. When mixed together in solution, random noncovalent copolymers are formed that contain all three types of chromophores, resulting in energy transfer upon excitation of the oligofluorene energy donor. At a certain mixing ratio, a white emissive supramolecular polymer can be created in solution. In contrast to their unfunctionalized counterparts, bis-UPy-chromophores can easily be deposited as smooth thin films on surfaces by spin coating. No phase separation is observed in these films, and energy transfer is much more efficient than in solution, giving rise to white fluorescence at much lower ratios of energy acceptor to donor. Light emitting diodes based on these supramolecular polymers have been prepared from all three types of pure materials, yielding blue, green, and red devices, respectively. At appropriate mixing ratios of these three compounds, white electroluminescence is observed. This approach yields a toolbox of molecules that can be easily used to construct π-conjugated supramolecular polymers with a variety of compositions, high solution viscosities, and tuneable emission colors.

Introduction

White emitting plastic materials[1,2] are attractive candidates for applications in flexible full-color light-emitting diodes (LEDs) and in backlights for liquid-crystalline displays.[3−5] A common approach to obtain these materials is based on polymers blended with luminescent dyes that simultaneously emit over the whole visible range due to partial energy transfer from energy donor polymers to acceptor dyes.[6−11] Chen et al. have expanded this principle to create linearly polarized white light based on aligned fluorene oligomers.[12] Alternatively, copolymers containing moieties emitting at different wavelengths have been employed to avoid phase separation of the polymer and the dye.[13−16] Recently, a supramolecular concept has been reported by Ajayaghosh and co-workers in which a π-conjugated polymer was encapsulated in a π-organogel.[17,18] At a specific composition and temperature, partial energy transfer from the gel to the polymer resulted in white photoluminescence. However, white light emitting thin films and electroluminescent devices based on supramolecular interactions such as hydrogen bonding, $\pi-\pi$-stacking, or solvophobic effects have never been reported.

The creation of multicomponent π-conjugated systems[18−20] by a supramolecular approach combines the advantages of small

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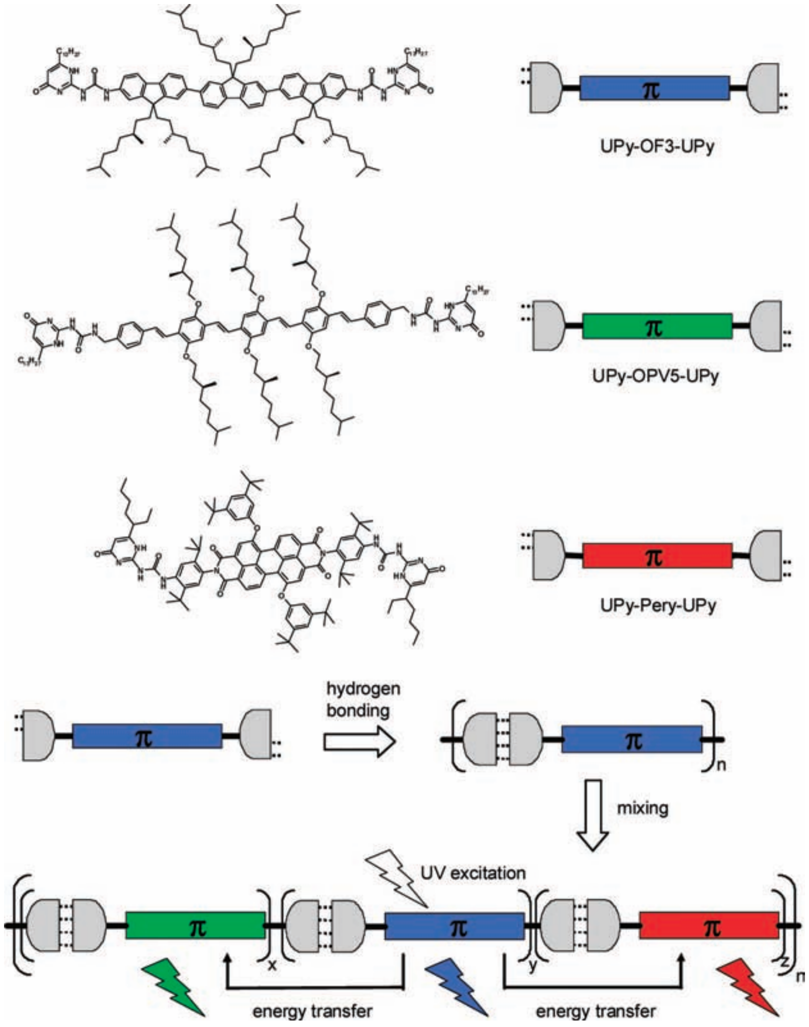
10.1021/ja807996y CCC: $40.75

Chart 1. Chemical Structures of the di-UPy Functionalized Chromophores Used in This Study and a Schematic Illustration of the Creation of White Photoluminescence



molecules with those of polymers and allows us to influence the morphology and phase separation through noncovalent interactions.[21] Self-assembled electroactive multicomponent systems in which a close spatial proximity and controlled orientation between the different species facilitates electronic processes such as electron transfer,[22] singlet–singlet,[23–26] or triplet–triplet[27] energy transfer, have been reported. In the past, we have synthesized blue emissive oligofluorenes (OF)[25] equipped with quadruple hydrogen bonding 2-ureido-4[1*H*]-pyrimidinone[28,29] (UPy) end groups. These molecules self-assembled into supramolecular polymers and could be dynamically end-capped with energy acceptor molecules by adding mono-UPy green- and red-emissive end cappers. Due to the self-complementarity of the UPy units, these systems inevitably contained a fraction of homodimers of hydrogen bonded acceptors, which reduced the energy transfer efficiency. Additionally, the virtual molecular weight was significantly decreased with increasing end capper concentration. This problem should in principle be solved by using exclusively difunctionalised UPy chromophores, avoiding acceptor homodimers and leaving the virtual molecular weight unchanged. Complications to this approach might, however, arise from ring-chain equilibria because at low concentrations supramolecular polymers are known to exist preferably as cycles, whereas at higher concentrations linear polymers are formed.[30,31]

Here, we report our results of this novel concept by using three difunctionalized UPy chromophores: a blue emitting OF (**UPy-OF3-UPy**), a green emitting OPV (**UPy-OPV5-UPy**), and a red emitting PB (**UPy-Pery-UPy**) to create red-green-blue (RGB) supramolecular materials (Chart 1). In a mixed system of these hydrogen bonded copolymers the formation of acceptor

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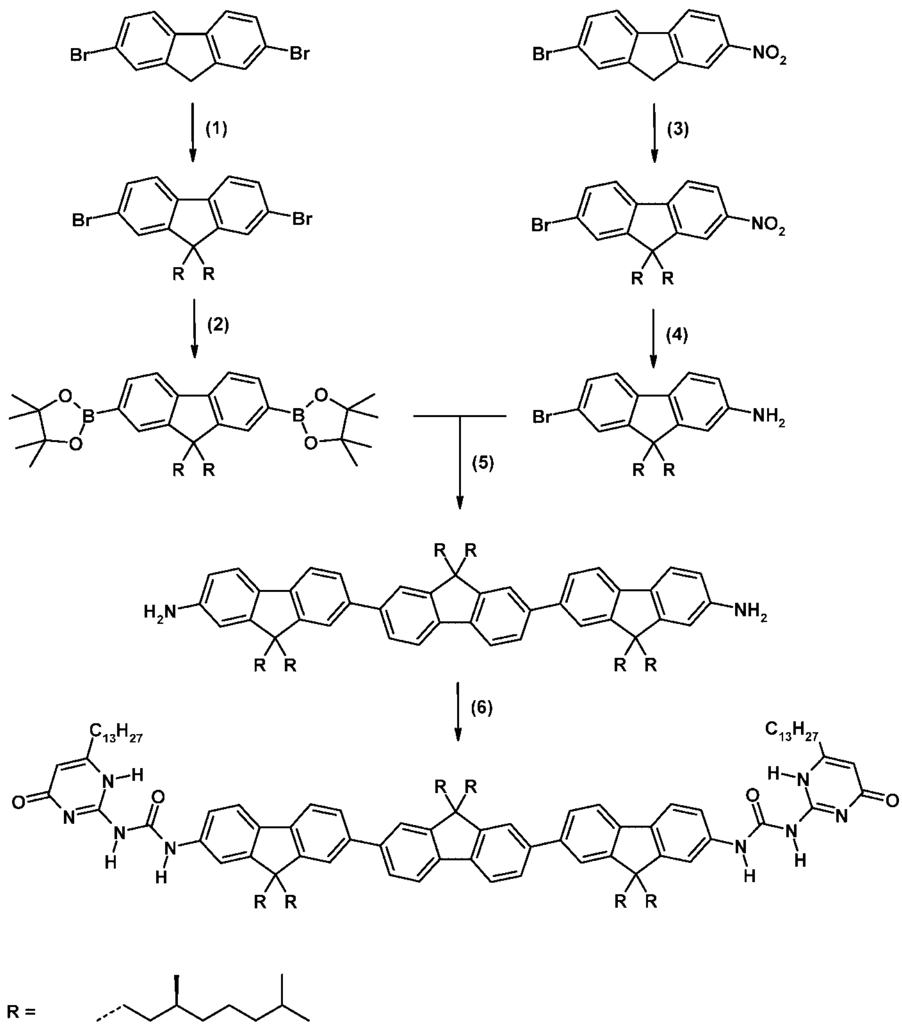
Scheme 1. Synthesis of **UPy-OF3-UPy**[a]



[a] (1) (*S*)-3,7-Dimethyloctylbromide, DMSO/aq. NaOH, benzyltriethyl ammonium bromide, overnight, RT, 74 − 95%. (2) THF, 1. *n*BuLi, 2. isopropoxypinacolatoborolane, 1 h, −78 °C, 64%. (3) (*S*)-3,7-Dimethyloctylbromide, DMSO/KOH, KI, overnight, RT, 58%. (4) $SnCl_2$, EtOH/EtOAc, Ar, 3d, reflux, 93%. (5): $Pd(PPh_3)_4$, Na_2CO_3, dioxane/water (2:1), Ar, 3d, 90 °C, 55%. (6) CDI activated tridecylisocytosine, $CHCl_3$, Ar, overnight, reflux, 56%.

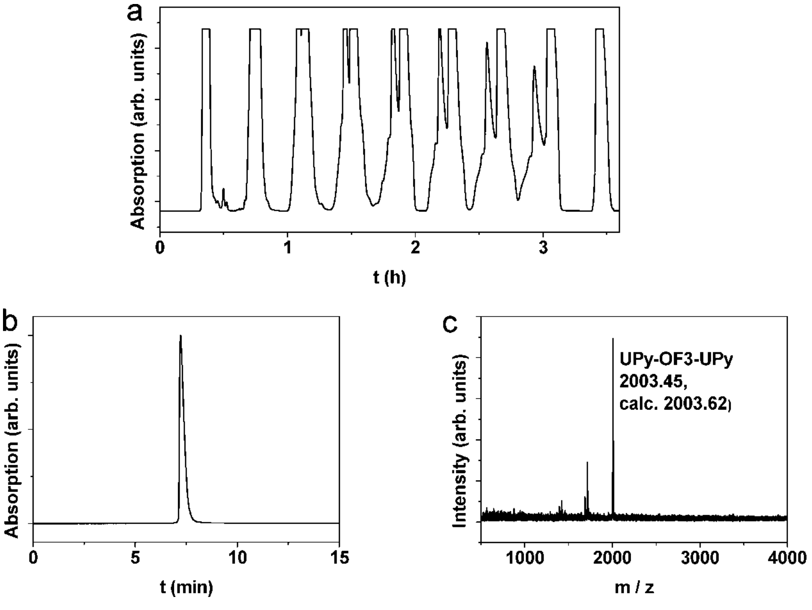


Figure 1. (a) Recycling GPC trace of **UPy-OF3-UPy** in THF + 1% TFA. (b) Analytical GPC trace of **UPy-OF3-UPy** in THF after recycling GPC. (c) MALDI-TOF mass spectrum of **UPy-OF3-UPy**. The small peaks at lower *m*/*z* values are due to fragmentation of the N−C bonds of the urea moieties.

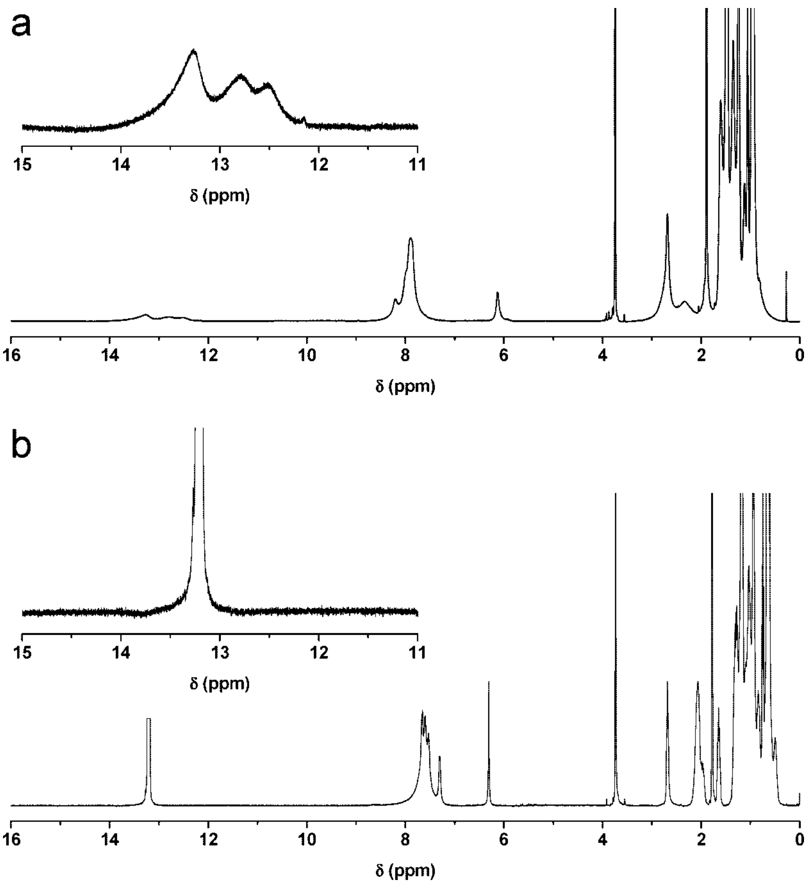


Figure 2. Full ^{1}H NMR spectra and magnification of the hydrogen bonding region (inset) of **UPy-OF3-UPy** in THF-d_8 (a) and in THF-d_8 containing ca. 30 vol% TFA-d_1 (b). The peak at ca. 13.2 ppm in Figure 2b is due to TFA.

dimers could be successfully avoided, whereas the virtual molecular weight was affected by the formation of cyclic structures. Nevertheless, the degree of polymerization was sufficiently high to create white photoluminescent supramolecular polymers both in solution and in spin coated films. Finally, we succeeded in applying these materials in white light emitting diodes (LEDs).

Results and Discussion

Synthesis, Purification, and Characterization. Based on the expertise in our group,[22−25] we chose a perylene bisimide (PB), an oligo(phenylene-vinylene) (OPV), and an oligofluorene (OF) as the RGB emissive bis-UPy chromophores. In the case of the OFs, a series of di- and monosubstituted UPy compounds of various conjugation lengths (up to five) was prepared based on our earlier reported synthetic procedure[25] for 9,9′-dihexylfluorene derivatives (Scheme 1 and Supporting Information). In the present study we will focus on the trimer **UPy-OF3-UPy** as the blue emissive species.

After conventional workup (silica column chromatography), it was evident from MALDI-TOF, ^{1}H NMR, and GPC analysis[32] that the final product **UPy-OF3-UPy** still contained some impurities. Therefore it was subjected to recycling GPC[33] (Figure 1). Using this technique, the compound was obtained in high purity (>99%), as was confirmed by MALDI-TOF, ^{1}H NMR, and analytical GPC.

After recycling GPC, **UPy-OF3-UPy** was obtained as a light orange solid that showed a rather limited solubility in common organic solvents (chloroform, THF, toluene) under ambient conditions. Concentrated solutions (in the mM regime and above) could only be reached by heating, by addition of strong hydrogen bond breaking additives, such as TFA,[25] or by using *o*-dichlorobenzene (ODCB) as the solvent.

^{1}H NMR experiments revealed association of the UPy groups in THF-d_8 (Figure 2). The solutions were very viscous and peak broadening in the whole spectrum was observed, pointing to the presence of aggregates of high virtual molecular weight. Three weak signals that were strongly shifted upfield (δ 12.5, 12.8, and 13.3 ppm) indicated the presence of quadruple hydrogen bonds, and in agreement with the high association constant,[28] no unbound UPy groups could be detected. Also, the only NMR peaks observed corresponded to the pyrimidinone tautomer, and no enol form[28] was found. Upon addition of TFA-d_1, the viscosity of the solution strongly decreased, the NH

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(32) It should be mentioned that the resolution of the analytical GPC chromatograms very strongly depended on the solvent used. In chloroform, which is a good solvent for unfunctionalised oligofluorenes, strong tailing of the peaks prevented efficient separation, whereas, in THF, separation was possible on an analytical scale without further additives.

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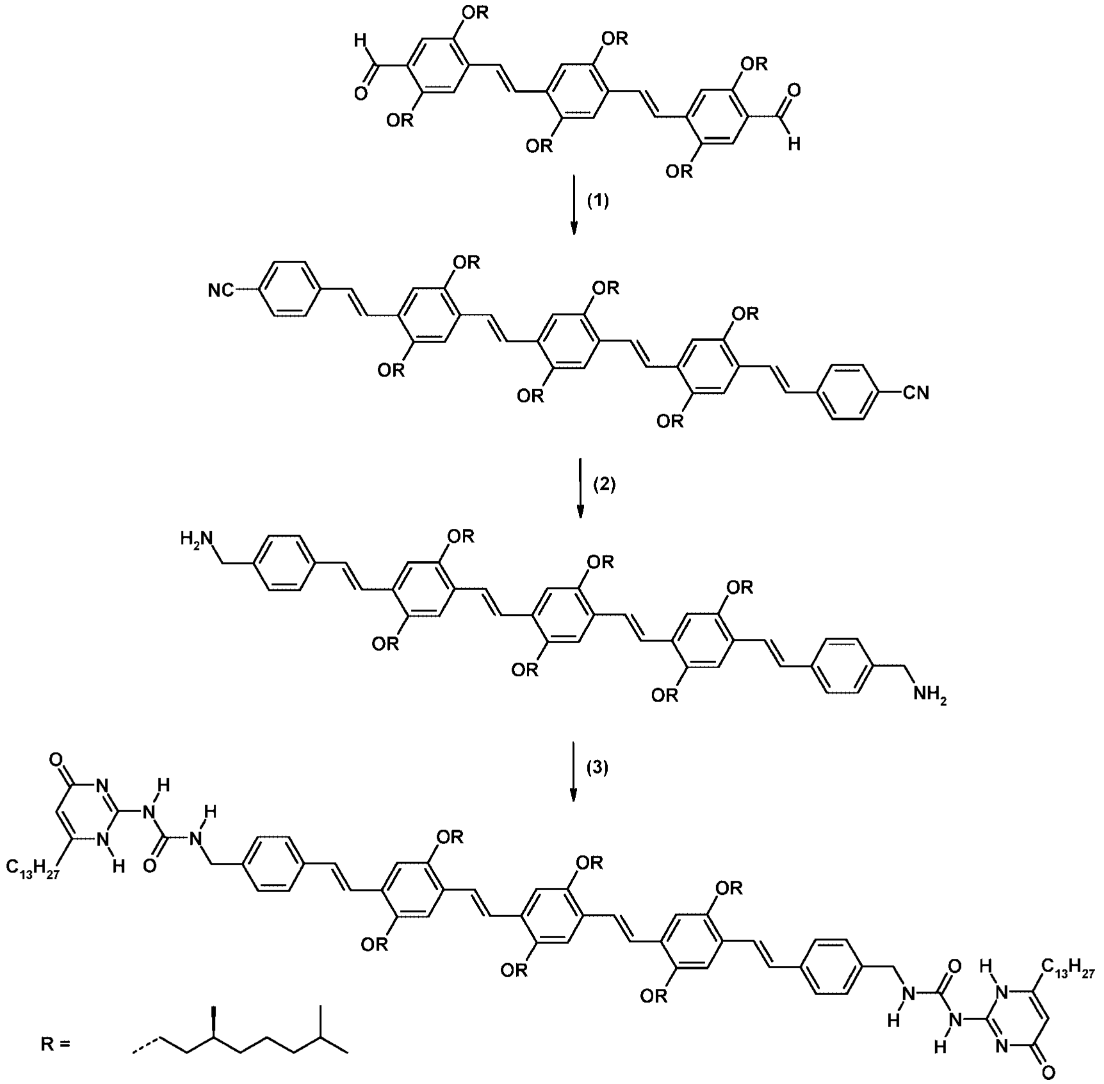
Scheme 2. Synthesis of **UPy-OPV5-UPy**[a]



[a] (1) KO^{t}Bu, 4-cyanobenzyldiethylphosphonate, DMF/THF, overnight, RT, 85%. (2) $LiAlH_4$, Et_2O, overnight, RT, 90%. (3) CDI activated tridecylisocytosine, $CHCl_3$, reflux, overnight, 25%.

protons disappeared from the spectrum due to exchange with deuterium, and the residual peaks sharpened, indicating that the compound was not hydrogen bonded any more.

Green-emitting **UPy-OPV5-UPy** was prepared by stepwise Wittig couplings of benzyl triphenylphosphonium salts and aromatic aldehydes[34] and subsequent reduction of the peripheral cyano groups to benzyl amines, which finally were reacted with an activated isocytosine derivative[35] to yield the di-UPy compound (Scheme 2 and Supporting Information). Similar to the case described for **UPy-OF3-UPy**, conventional purification procedures did not suffice to obtain the product in a pure form, but recycling GPC enabled us to reach a high purity level (<99%). The yellow-orange solid is well soluble in a variety of organic solvents.

UPy-Pery-UPy was synthesized in analogy to the corresponding mono-UPy derivative[25] by reaction of an diaryloxy substituted perylene anhydride[36] with excess 1,4-diamino-2,6-di-*tert*-butylbenzene and subsequent coupling with activated isocytosine analogous to the OPV and OF derivatives[37] (Scheme 3 and Supporting Information). We found that after column chromatography the only impurity present was the 1,6-diphenoxy isomer[38] (ca. 10%). As it was very difficult to remove and not expected to influence the electronic properties of the material significantly, no further purification was performed. The final product is a dark red solid and dissolves well in a variety of organic solvents. In contrast to **UPy-OF3-UPy**, its NMR spectrum in THF-d_8 shows rather sharp peaks already without the addition of TFA-d_1 (Supporting Information).

Chloroform solutions (μM regime) of **UPy-OPV5-UPy** and **UPy-Pery-UPy** showed absorption spectra that were typical for these types of chromophore[39−43] (Table 1 and Figure 3).

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(37) It should be noted that, due to solubility reasons, the UPy groups in **UPy-Pery-UPy** were substituted with a racemic ethylpentyl chain, whereas straight tridecyl chains were used for **UPy-OF3-UPy** and **UPy-OPV5-UPy**. No racemic substituents were used in these latter two cases to exclude the formation of diastereomers.

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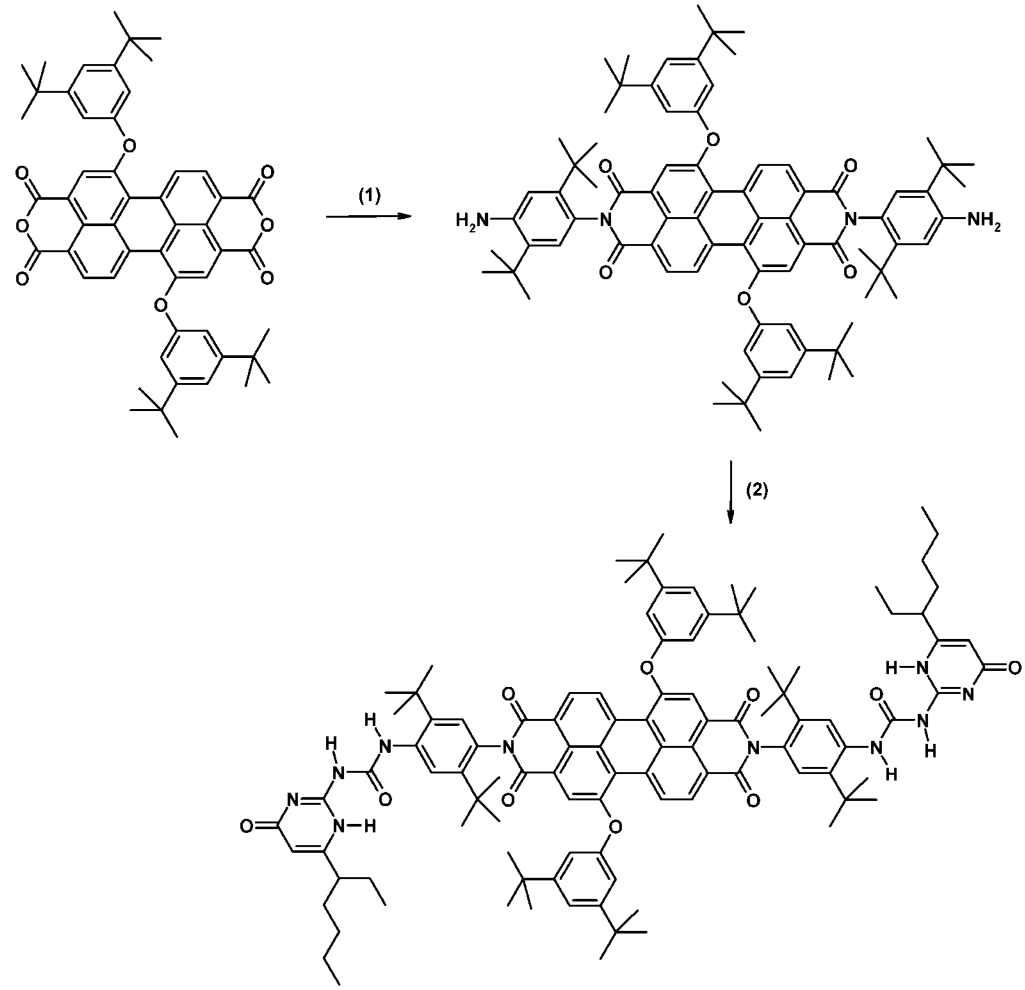
Scheme 3. Synthesis of **UPy-Pery-UPy**[a]



[a] (1) 1,4-Diamino-2,6-di-*tert*-butylbenzene, Zn acetate, DMA, 190 °C, 3 h, 60%. (2) CDI activated ethylhexylisocytosine, $CHCl_3$, reflux, 18 h, 97%.

Table 1. Optical Properties of **UPy-OF3-UPy**, **UPy-OPV5-UPy**, and **UPy-Pery-UPy** in Diluted Chloroform Solution

	λ_{max}^{Abs} (nm)	log(ϵ) (M^{-1} cm^{-1})	λ_{max}^{PL} (nm)	ϕ_{PL}[a] (%)
UPy-OF3-UPy	364	4.91	407, 429	50
UPy-OPV5-UPy	445	4.90	520, 554	45
UPy-Pery-UPy	513, 550	4.57, 4.70	584, 620	55

[a] Reference compounds: 9,10-diphenylanthracene in cyclohexane (for **UPy-OF3-UPy**), *N*,*N*′-bis(pentylhexyl) perylene bisimide in dichloromethane (for **UPy-OPV5-UPy**) and Rhodamine 101 in ethanol (for **UPy-Pery-UPy**).

Compared to unfunctionalized trifluorenes,[44,45] the spectrum of **UPy-OF3-UPy** was red-shifted by ca. 15 nm, presumably due to the electron-donating influence of the UPy group, which is directly conjugated to the aromatic core.[25] Upon excitation at their maximum absorption energies all three compounds emitted visible light with fluorescence quantum yields of ~50% (Table 1). All photoluminescence spectra consisted of two maxima and a shoulder at the low energy end (Figure 3). In accordance with the changes in the optical band gaps, the emission colors shifted from blue for **UPy-OF3-UPy** to green for **UPy-OPV5-UPy** and to red for **UPy-Pery-UPy**. As in the case of the absorption spectra, the observed photoluminescence features were typical for the respective conjugated systems,[39−43] with a 15 nm red shift for **UPy-OF3-UPy**.[44,45] These results indicated that the beneficial fluorescence properties of the chromophores were preserved upon functionalization with the hydrogen bonding end groups.

Energy Transfer Studies in Solution. Before we started with energy transfer between the di-UPy chromophores, we first determined the UPy dimerization constant for our type of systems in an energy transfer dilution experiment. To simplify the calculations, the monofunctional UPy analogues **UPy-OF3** and **UPy-OPV4**[25] (Figure 4a) were used instead of **UPy-OF3-UPy** and **UPy-OPV5-UPy**, because they formed exclusively dimers. As expected, quenching of the blue oligofluorene emission was observed already after addition of small amounts of acceptor, indicating the close spatial proximity of **UPy-OPV4** and **UPy-OF3** due to the formation of heterodimers[23] (Figure

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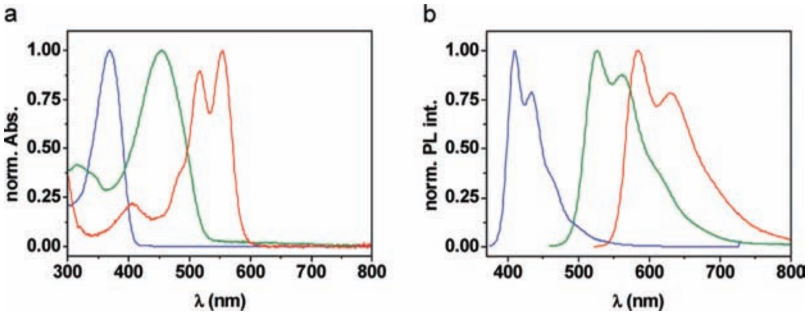

Figure 3. Normalized absorption (a) and fluorescence (b) spectra of diluted (μM regime) solutions of **UPy-OF3-UPy** (blue), **UPy-OPV5-UPy** (green), and **UPy-Pery-UPy** (red) in chloroform.

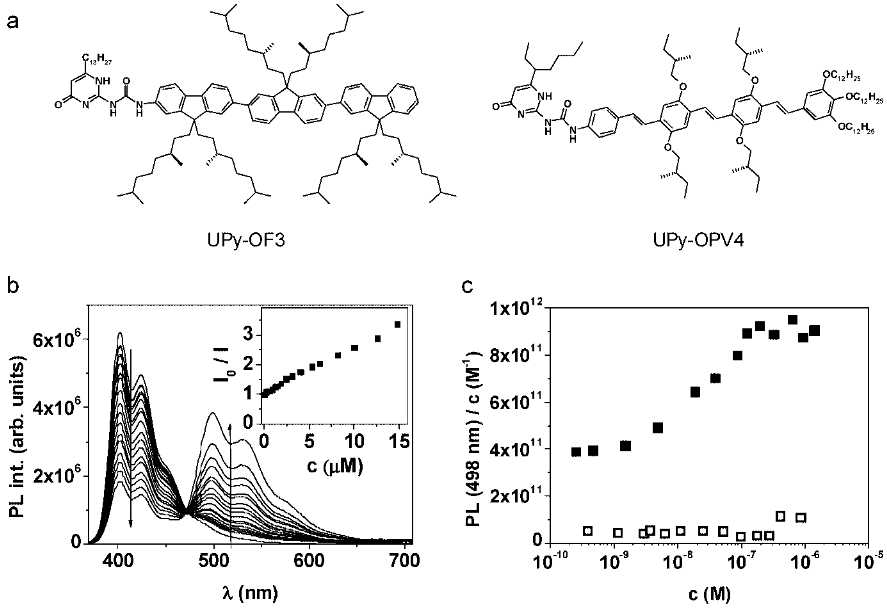

Figure 4. (a) Structural formulas of **UPy-OF3** and **UPy-OPV4**. (b) Fluorescence titration experiment between **UPy-OF3** and **UPy-OPV4** with constant donor concentration (8.8×10^{-6} M) in $CHCl_3$. Arrows indicate the spectral changes upon increasing the concentration of **UPy-OPV4**. Excitation wavelength $\lambda_{exc} = 359$ nm. The inset shows the corresponding Stern−Volmer plot. (c) Concentration dependence of acceptor emission in an equimolar mixture of **UPy-OF3** and **UPy-OPV4** (■) and **UPy-OF3** and an unfunctionalised OPV4 (□), see Supporting Information. Excitation wavelength $\lambda_{exc} = 359$ nm.

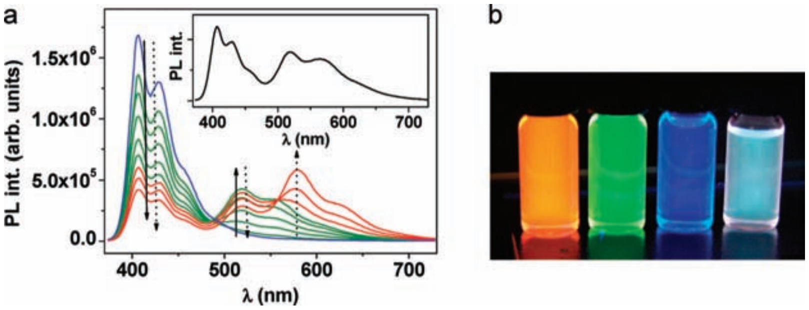

Figure 5. (a) Titration experiment in chloroform solution (blue: pure **UPy-OF3-UPy**, green: successive addition of **UPy-OPV5-UPy**, red: further addition of **UPy-Pery-UPy**). The solid arrows indicate spectral changes upon addition of **UPy-OPV5-UPy** to **UPy-OF3-UPy**, the dotted arrow upon addition of **UPy-Pery-UPy** to a mixture of **UPy-OF3-UPy** and **UPy-OPV5-UPy**. The inset shows the spectrum corresponding to a ratio of 59:33:8. c(**UPy-OF3-UPy**) $= 1.6 \times 10^{-6}$ M. Excitation wavelength $\lambda_{exc} = 364$ nm. (b) Solutions of pure di-UPy chromophores and a white emitting mixture in chloroform under UV irradiation ($\lambda_{exc} = 365$ nm).

4b). The dimerization constant was determined by dilution of an equimolar mixture of **UPy-OF3** and **UPy-OPV4** and recording its fluorescence spectra at various concentrations (Figure 4c). A decrease in acceptor emission and thus in energy transfer efficiency was observed upon dilution below 10^{-7} M. The contribution of direct excitation could be neglected, since a control experiment with an unsubstituted OPV showed hardly any OPV fluorescence. Assuming equal probability for the formation of UPy dimers between identical and different chromophores (corresponding to 50% of heterodimers and 25% of each type of homodimer), we could extract a dimerization constant of 2×10^7 M^{-1} from the data. This value is in good agreement with results reported for other UPy systems in chloroform[28] and high enough to ensure that, at the concentrations used in the following experiments (10^{-6}−10^{-5} M), the bisUPy compounds were present exclusively as hydrogen

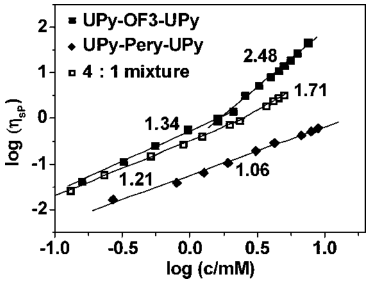

Figure 6. Double logarithmic plot of specific viscosity vs concentration of **UPy-OF3-UPy**, **UPy-Pery-UPy**, and a 4: 1 mixture of both compounds in ODCB. Numbers indicate the slopes of the linear fits.

bonded species. Based on previous data for UPy supramolecular polymers,[30,31,46] it could be anticipated that under these conditions the rigid **UPy-OF3-UPy** and **UPy-OPV5-UPy**, in which the UPy groups are arranged at an angle of less than 180°, were present as cycles rather than linear polymers. By contrast, such ring formation should be excluded for **UPy-Pery-UPy**, owing to the strictly linear array of its UPy functionalities.

In fluorescence titration experiments of **UPy-OF3-UPy** with either **UPy-OPV5-UPy** or **UPy-Pery-UPy** (Supporting Information), quenching of the donor emission was observed when the samples were excited at the maximum absorption wavelength of **UPy-OF3-UPy** ($\lambda_{\mathrm{exc}} = 364$ nm). Simultaneously, the emission of the acceptor molecules increased. Quenching of the donor fluorescence, as expressed by the Stern–Volmer constants (K_{SV}), was higher when the spectral overlap (J_{F}) between the donor emission and the acceptor absorption was better ($J_{\mathrm{F}} = 2 \times 10^{15}$ nm^4 M^{-1} cm^{-1} and $K_{\mathrm{SV}} = 7.2 \times 10^6$ M^{-1} for **UPy-OPV5-UPy** vs $J_{\mathrm{F}} = 5 \times 10^{14}$ nm^4 M^{-1} cm^{-1} and $K_{\mathrm{SV}} = 3.5 \times 10^6$ M^{-1} for **UPy-Pery-UPy** as the acceptor). Both K_{SV} values were more than doubled compared to the case of our earlier reported titrations of di-UPy-trifluorene with mono-UPy OPV or PB acceptor molecules ($K_{\mathrm{SV}} = 2.9 \times 10^6$ M^{-1} and $K_{\mathrm{SV}} = 1.3 \times 10^6$ M^{-1}, respectively).[25] Since the chromophores in both experiments were similar, the spectral overlap was comparable for the mono- and di-UPy derivatives. Therefore, the higher K_{SV} found in the present study was due to the increased probability for an energy acceptor to be bound to a donor as a result of the absence of acceptor or donor homodimers.

Simultaneous incorporation of **UPy-OPV5-UPy** and **UPy-Pery-UPy** into the **UPy-OF3-UPy** chains led to a proposed supramolecular copolymer containing all three species even at very low concentrations (μM regime). When **UPy-Pery-UPy** was titrated to a mixture containing **UPy-OF3-UPy** and **UPy-OPV5-UPy** at a constant ratio (64:36), both green (OPV) and remaining blue (OF) emissions were quenched. At a certain ratio (**UPy-OF3-UPy/UPy-OPV5-UPy/UPy-Pery-UPy** = 59:33:8), simultaneous photoluminescence of comparable intensity over the whole visible spectrum could be achieved, leading to white emission (Figure 5) due to partial energy transfer. The relatively high ratio of **UPy-OPV5-UPy** to **UPy-OF3-UPy** suggested that cascade energy transfer took place in which **UPy-OPV5-UPy** also acted as an energy donor for **UPy-Pery-UPy**. By contrast, white emission could not be achieved using mixtures of bare OF, OPV, and PB chromophores that lack the UPy units.[25]

Viscosimetry. Before spin coating solutions of the di-UPy chromophores, we conducted viscosimetric experiments to investigate if the virtual molecular weight of **UPy-OF3-UPy** was affected by the incorporation of the energy acceptors. These measurements were carried out in the concentration range later used for spin coating (mM regime; *vide infra*) because a certain solution viscosity was crucial to yield thin films of a typical thickness (ca. 50 nm) required for LED applications. Due to the limited solubility of **UPy-OF3-UPy** in chloroform we chose ODCB instead, since it is a good solvent for **UPy-OF3-UPy** and frequently used for spin coating (Figure 6).[47] For the viscosimetry experiments, the specific viscosities of solutions were measured as a function of concentration. In the case of **UPy-OF3-UPy**, a double logarithmic plot gave a slope of 1.34 at low and of 2.48 at high concentrations with an inflection point at 2 mM. By contrast, **UPy-Pery-UPy** gave a linear dependence with a slope of only 1.06 over the whole concentration range investigated. Since all UPy groups were hydrogen bonded and a slope close to 1 is indicative of noninteraction particles of constant size,[31] we concluded that **UPy-Pery-UPy** must be primarily present as hydrogen bonded cycles. Based on its rigid molecular structure in which the UPy groups are arranged in a fixed angle of 180°, this behavior is surprising. Instead, the formation of linear polymers seems more likely. A possible explanation might be that the UPy groups do not dimerize in a planar but slightly bent fashion. In the case of **UPy-OF3-UPy**, in which the UPy groups are arranged at an angle smaller than 180°, most likely rings also were present below 2 mM. The slope 1.34 at low concentrations might be explained either by rings that aggregate further by secondary interactions other than hydrogen bonding[48] or by an increase in the cycle size with concentration. At higher concentrations the strong increase in viscosities is probably due to a transition to linear polymers, as is frequently found in other di-UPy systems.[30,31,46] Our results demonstrate that the virtual molecular weights for both systems were remarkably different, although both consisted entirely of difunctionalized molecules. A mixture of **UPy-OF3-UPy** and **UPy-Pery-UPy** in a 4:1 ratio exhibited viscosities intermediate between the two pure compounds. It still changed the slope at ca. 2 mM, but both the slopes at concentrations below and above this threshold were lower than in the case of pure **UPy-OF3-UPy**.

Spin Coated Films. When spin coated from concentrated ODCB solution (4.5–9 mM) all di-UPy compounds were found to form smooth homogeneous thin films[49] with surface roughnesses of 5 nm or below, as was shown by atomic force microscopy (Supporting Information). This result proved that the hydrogen bonded chromophores could be successfully spin coated even at concentrations where the ring-chain equilibria were shifted toward cycles, which might indicate that the rings were large enough to be easily deposited in the same fashion as a polymer. Alternatively, the rather low volatility of the ODCB might have allowed additional polymerization of the cyclic oligomers during the deposition process. By contrast, the mono-UPy compounds used to determine the UPy dimerization

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(46) Söntjes, S. H. M.; Sijbesma, R. P.; van Genderen, M. H. P.; Meijer, E. W. *Macromolecules* **2001**, *34*, 3815.

(47) Fluorescence energy transfer titration studies in diluted ODCB solutions (mM regime) gave a similar Stern–Volmer constant as determined in chloroform solution for energy transfer from **UPy-OF3-UPy** to **UPy-Pery-UPy** ($K_{\mathrm{SV}} = 3.2 \times 10^6$ M^{-1} vs 3.5×10^6 M^{-1}; see Supporting Information). Since K_{SV} reflects the dimerization constant between the UPy units, we expected comparable values in both solvents.

(48) A specification of the type of secondary interaction that accounts for the additional aggregation is not possible at the moment, but π-stacking interactions are rather unlikely to be the case, as they should be accompanied by characteristic shifts in both NMR and optical spectra, which were absent in our systems.

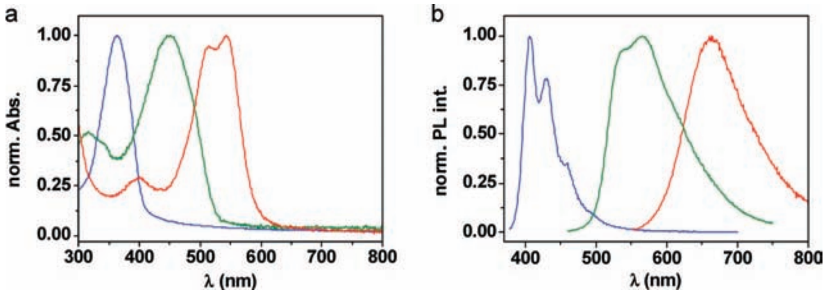

Figure 7. Normalized absorption (a) and fluorescence (b) spectra of thin films of **UPy-OF3-UPy** (blue), **UPy-OPV5-UPy** (green), and **UPy-Pery-UPy** (red) spin coated from ODCB solutions.

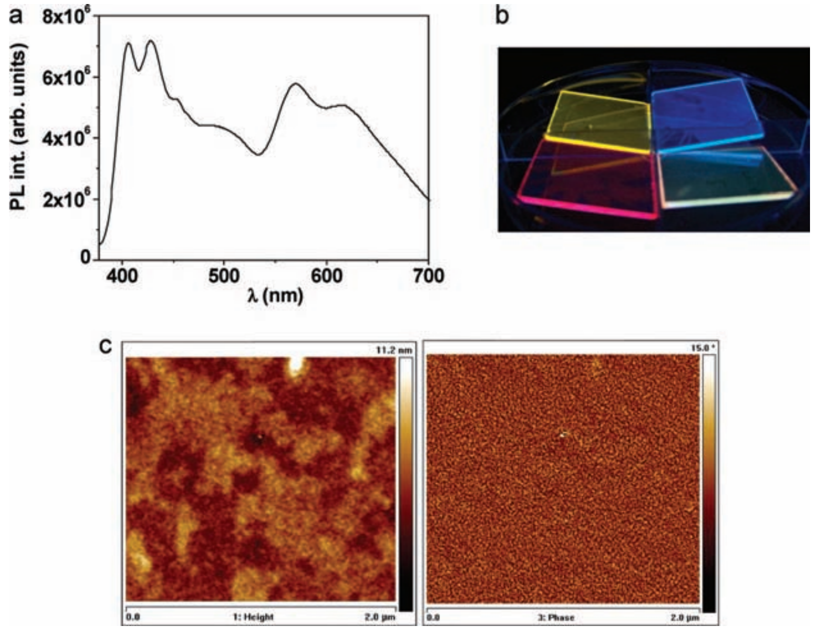

Figure 8. (a) Simultaneous photoluminescence of all three di-UPy chromophores (ratio 84:10:6) in a thin spin coated film. Excitation wavelength $\lambda_{\text{exc}} =$ 365 nm. (b) Thin spin coated films of pure di-UPy chromophores and a mixture under UV irradiation (365 nm). (c) AFM height (left) and phase (right) images of thin film spin coated from a 80:10:10 mixture of the three chromophores. The z-scale corresponds to a height of 10 nm.

constant (Figure 4a) formed very inhomogeneous films, indicating that it is necessary to have bis-UPy chromophores.

The UV absorption and photoluminescence spectra of the **UPy-OF3-UPy** spin coated films strongly resembled those in solution (see Figure 3), and the film was blue emissive (Figure 7). Compared to their solution spectra, the fluorescence maxima of **UPy-OPV5-UPy** and **UPy-Pery-UPy** in the films were shifted to lower energies and exhibited a rather broad emission band, but their emission colors were still in the appropriate color regime (Figure 7). This set of di-UPy chromophores enabled us to prepare RGB emissive supramolecular materials.

Energy Transfer Studies in Thin Films. To create white emissive materials by partial energy transfer, various mixtures of the three components in ODCB were spin coated onto quartz substrates. AFM images of the obtained films showed very smooth, featureless surfaces that closely resembled those of the pure components. No indications of phase separation could be found at various compositions, suggesting that supramolecular statistical copolymers were present in these mixed films (Figure 8 and Supporting Information). Fluorescence quenching of the OF emission was observed at much lower acceptor-to-donor ratios than in dilute solution, indicating more pronounced energy transfer in the films due to the narrower packing of the chromophores (Supporting Information). Compared to the photoluminescence spectra of the pure materials, the emission maxima of both energy acceptors were shifted significantly to the blue in the mixed films ($\Delta\lambda = 80-90$ nm). The sensitized acceptor fluorescence was reminiscent of that of hydrogen bonded species in solution (Table 1), implying the presence of isolated acceptors inside the donor assemblies.[50] This is further evidence for random copolymers being present in the films instead of phase separated domains. As the photoexcitation took place at the absorption maximum of the energy donor (375 nm), where also both acceptor molecules absorbed, direct excitation contributed to some extent to the observed fluorescence spectra, as was confirmed by excitation spectroscopy (Supporting Information). A white photoluminescent film (CIE coordinates of 0.33 and 0.31; Figure 8) was achieved with a mixture of the chromophores in a ratio of **UPy-OF3-UPy/UPy-OPV5-UPy/UPy-Pery-UPy** = 84:10:6.

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(49) The film thickness was too small to allow infrared spectra to be recorded, but as powder samples showed a characteristic band at ca. 1700 cm^{-1}, the assumption was supported that in the solid state and thus also in spin coated films hydrogen bonded UPy keto tautomers were the predominant species.

(50) Hoeben, F. J. M.; Herz, L. M.; Daniel, C.; Jonkheijm, P.; Schenning, A. P. H. J.; Silva, C.; Meskers, S. C. J.; Beljonne, D.; Phillips, R. T.; Friend, R. H.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 1976.

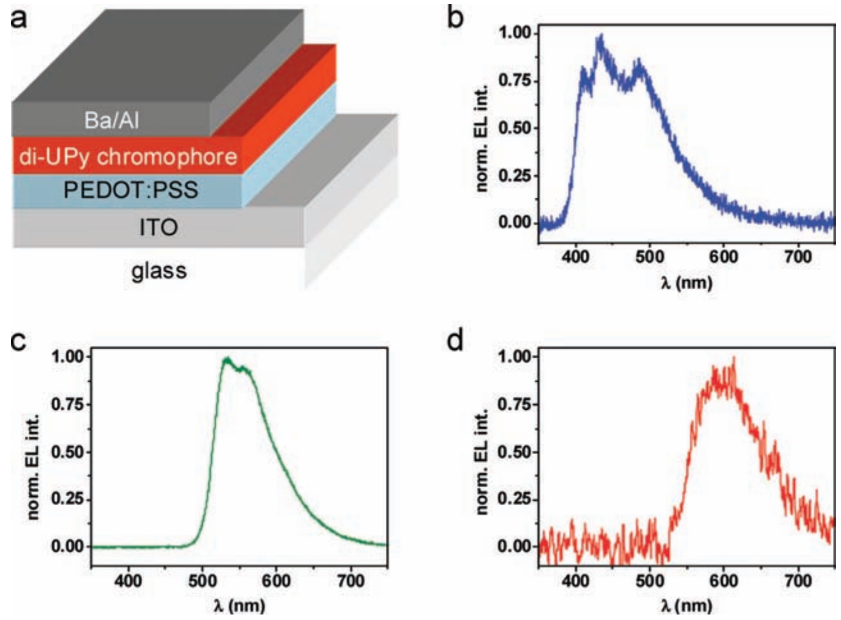

Figure 9. Device architecture of the OLEDs (a) and normalized electroluminescence spectra of **UPy-OF3-UPy** (b), **UPy-OPV5-UPy** (c), and **UPy-Pery-UPy** (d).

Table 2. Summary of the Device Characteristics

compound	λ_{max}(nm)	max. intensity (cd/m^2)	efficiency (cd/A)	turn-on voltage (V)
UPy-OF3-UPy	410, 435, 485	32	0.025	7.4
UPy-OPV5-UPy	534, 553	210	0.051	4.5
UPy-Pery-UPy	600	-	-	-

Electroluminescent Devices. The three chromophores were employed as the active materials in layered electroluminescent diodes constructed of a glass substrate, transparent ITO electrodes, PEDOT/PSS, spin coated films of the di-UPy compounds, and electrodes of barium (5 nm) and aluminum (100 nm). In all cases light emission could be observed when a sufficiently high voltage was applied (Figure 9, Table 2 and Supporting Information), which proves that the presence of UPy groups in these LEDs is not detrimental for their performance. With the highest intensity and efficiency, the lowest turn-on voltage, and yellow-green electroluminescence closely resembling those in its PL spectrum, **UPy-OPV5-UPy** exceeded the device characteristics of the other two compounds. **UPy-OF3-UPy** gave somewhat less propitious values, and aside from its typical blue emission, also a significant contribution in the green region was found. This low energy emission is diagnostic for fluorenone defects.[51−53] As the material had been purified extensively by recycling GPC, any chemical contamination should have been removed,[33] which was also supported by the absence of green emission in the PL spectrum of **UPy-OF3-UPy**. Therefore we suppose that the degradation took place during device operation.[54] The devices containing **UPy-Pery-UPy** had a low performance, although at high voltages red emission could be detected. Current−voltage curves measured under reverse and forward bias, however, revealed that the measured currents were almost completely due to leakage and hardly any charge injection took place.[55]

In the electroluminescence spectra of mixed systems, even lower acceptor concentrations than in the photoluminescence of mixed films were sufficient to obtain simultaneous emission (Figure 10 and Table 3). This effect could be caused by direct injection of charges into the **UPy-OPV5-UPy** at the voltages used during operation (up to 24 V). As in the case of the fluorescence spectra, the luminescence of **UPy-OPV5-UPy** embedded in a matrix of **UPy-OF3-UPy** was reminiscent of nonaggregated molecules. At appropriate mixing ratios, it was possible to obtain an electroluminescence spectrum close to the CIE coordinates of white light. A small decrease in blue and an increase in green emission were observed when the percentage of **UPy-OPV5-UPy** was increased, with the CIE values changing correspondingly. This shows that partial energy transfer can be controlled by variation of the donor to acceptor ratios without changing film quality.

Conclusion

Three chromophores with emission spectra in the RGB wavelength region have been functionalized with self-complementary hydrogen bonding UPy groups at both ends, providing us with a novel toolbox of compounds for an easy modular approach toward supramolecular white emissive materials. Under appropriate conditions, these materials could be purified to a high extent by recycling GPC like small organic molecules. Depending on the concentration, hydrogen bonded cycles and linear polymers were observed in solution. Mixtures of the three chromophores gave white emissive supramolecular random copolymers without the formation of unwanted acceptor dimers.

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(51) Gamerith, S.; Gadermaier, C.; Scherf, U.; List, E. J. W. *Phys. Status Solidi A* **2004**, *201*, 1132.

(52) Montilla, F.; Mallavia, R. *Adv. Funct. Mater.* **2007**, *17*, 71.

(53) List, E. J. W.; Guentner, R.; Scanducci de Freitas, P.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374.

(54) Janssen, F. J. J.; van Ijzendoorn, L. J.; Schoo, H. F. M.; Sturm, J. M.; Andersson, G. G.; Dernier van der Gon, A. W.; Brongersma, H. H.; de Voigt, M. J. A. *Synth. Met.* **2002**, *131*, 167.

(55) Cyclic voltammetry in ODCB gave an HOMO energy of −6.2 eV (see Supporting Information), which is well below the work function of the ITO electrode (−5.2 eV) and therefore did not allow the injection of holes into the organic layer.

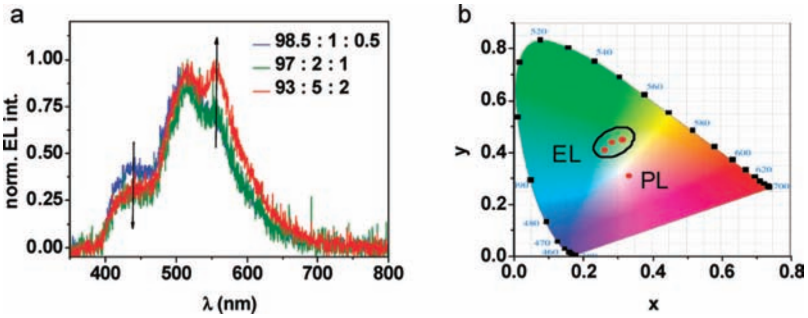

Figure 10. (a) Normalized electroluminescence spectra of mixtures of **UPy-OF3-UPy**, **UPy-OPV5-UPy**, and **UPy-Pery-UPy** at 24 V. The arrows indicate spectral changes upon decreasing percentrage of **UPy-OF3-UPy**. (b) Position of the EL and PL spectra in the CIE color space.

Table 3. CIE Values of the Device Emission Spectra for Mixed OLEDs of Various Compositions

UPy-OF3-UPy (mol %)	98.5	97.0	93.0
UPy-OPV5-UPy (mol %)	1.0	2.0	5.0
UPy-Pery-UPy (mol %)	0.5	1.0	2.0
CIE coordinates (*x*, *y*)	0.31, 0.45	0.28, 0.44	0.26, 0.41

Partial energy transfer was observed even in diluted solutions (μM regime) due to the high strength of the quadruple hydrogen bonding motif. Our modular approach allowed emission color tuning by simple mixing instead of labor-intensive synthesis of new materials. Binary and ternary mixtures exhibited high solution viscosities, which enabled us to apply spin coating to obtain homogeneous smooth films without phase separation. At appropriate ratios, partial energy transfer was observed, yielding white emissive films. Finally, these materials could be applied in solution processed OLEDs both as pure compounds and as mixtures. We have demonstrated the proof of principle that supramolecular polymers based on hydrogen bonded monodisperse chromophores can be applied successfully in organic light emitting diodes. In general, our modular approach is a promising strategy to create multicomponent systems that can be used as functional optoelectronic materials.

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Supporting Information Available: Synthetic procedures, experimental details and supporting figures that complement the article. This material is available free of charge via the Internet at http://pubs.acs.org.

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