π -Conjugated 2,2':6',2''-Bis(terpyridines): Systematical Tuning of the Optical Properties by Variation of the Linkage between the Terpyridines and the π -Conjugated System

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2,2':6',2''-Terpyridines bearing well-defined π -conjugated substituents at the 4'-position are known to exhibit interesting electronic and optical properties. The systematic variation of both the spacer unit and the linker in conjugated bis-(terpyridines) has resulted in a library of π -conjugated systems, enabling the study of the structure-property relationships of these materials. We have proven the Huisgen 1,3-dipolar cycloaddition reaction to be a versatile tool for connecting conjugated systems, even though the conjugation is hindered by the introduced triazole moiety. All the terpyrid-

Introduction

In recent years there has been an enormous growth of interest in the field of supramolecular architectures consisting of small molecules held together by weak, reversible, non-covalent interactions.^[1,2] Oligopyridyl ligands and their transition-metal complexes, which have found applications in several areas of modern research, are examples of such systems.^[3–13] 2,2':6',2''-Terpyridines bearing well-defined π -conjugated substituents at the 4'-position are known exhibit attractive electronic and optical properto ties.^[6,8,10,14-25] When two 2,2':6',2''-terpyridine units are introduced at either end of a rigid conjugated spacer, the resulting ditopic bis(terpyridine) ligand enables the synthesis of metallo-supramolecular polymers by coordination with different metal ions. Several publications dealing with the synthesis and characterization of such conjugated terpyrid-

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ine derivatives were fully characterized by ¹H and ¹³C NMR spectroscopy, UV/Vis absorption and emission measurements as well as MALDI-TOF MS. Thin films of the materials were produced by spin-coating and subsequently characterized. Because tuning of the band gap of the materials over a wide range is possible, quantum yields of up to 85 % and extinction coefficients of around 100000 M^{-1} cm⁻¹ could be observed, the compounds might be promising candidates for the design of new functional supramolecular materials.

ine systems have recently been published, but the spacer and/or connecting units utilized were generally not varied significantly nor in any systematic way.^[6,15,17,26,27] To enable the preparation of metallo-polymers exhibiting absorption over a wide range of the visible spectrum, we aimed to tune the band gap of our systems in an easy and systematic manner. The exchange of a phenyl moiety of the conjugated substituent by, for example, an anthracene or fluorene, enables the variation of the absorption of the derived terpyridyl system over a range of more than 100 nm. But not only the type of spacer unit affects the photophysical properties of these materials, but also the linker connecting the spacer to the terpyridine units, required for later introduction into supramolecular assemblies. This allows the synthesis of materials that show tailor-made optical properties. As a continuation of previous work in the field of π -conjugated terpyridines and their applications in supramolecular chemistry,^[27-29] in which we synthesized systems with different geometries^[30,31] and introduced the Huisgen reaction to the field of conjugated terpyridines,^[32] we have studied the effect of the systematic variation of both the spacer unit and the linker in conjugated bis(terpyridines). This should allow the elucidation of selected structure-property relationships of these materials. Furthermore, the knowledge gained by this investigation will facilitate the synthesis of materials that show tailor-made properties for applications in organic light-emitting diodes (OLEDs) and photovoltaic (PV) devices. This can be achieved by using a defined ratio of monomers showing complementary absorption spectra in combination with suitable transition-metal ions.



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Results and Discussion

Synthesis of Bis(terpyridines)

To investigate the influence of the electron-rich aromatic systems anthracene (9, 11 and 13) and fluorene (14–16) as part of the π -conjugated system in bis(terpyridines) and to determine differences with their phenyl-containing counterparts (8, 10 and 12), we initially synthesized the different conjugated spacer units by the approach shown in Scheme 1. The use of branched 2-ethylhexyl (EH) alkyl chains lead to soluble products, despite their linear and stiff geometry. By choosing different end-group functionalities we were able to investigate the effect of the connecting unit between the spacer and the terpyridine moiety. The general reaction scheme for the synthesis of the bis(terpyridines) T8–T16 by linking functionalized 4'-phenyl-2,2':6',2''-terpyridines 17 and 18 to the spacer units 8–16 is shown in Figure 1.



Scheme 1. Schematic representation of the structures and synthesis of the spacer units **8–16**.

By using halogen end-groups, the systems were coupled to a terpyridine derivative bearing an ethynyl functionality (17) by Sonogashira reaction to yield the conjugated bis(terpyridines) **T10**, **T11** and **T15**. The Huisgen 1,3-dipolar cycloaddition reaction^[33] under Cu^I catalysis, one of the socalled "click" reactions,^[34–38] was used to connect the terpyridine and the spacer in the cases of compounds **T12**, **T13** and **T16**. Again, **17** was used and "clicked" to the diazides of the aromatic systems synthesized in situ from the glycol



Figure 1. Schematic representation of the conversion of the conjugated spacer units **8–16** to bis(terpyridines) **T8–T16**.

boronates 12, 13 and $16^{[39]}$ These reactions were performed in a two-step one-pot procedure by first forming the azide at room temperature and then performing the Huisgen reaction at 100 °C using microwave heating. It was shown that both reactions can be carried out at room temperature, but under these conditions longer reaction times were required. Finally, the spacer was connected to the terpyridines through a C=C double bond by Horner–Wadsworth–Emmons (HWE) condensation of dialdehydes 8, 9 or 14 with a phosphonate-functionalized terpyridine (18)^[27] to yield the systems T8, T9 and T14.

All the terpyridine derivatives shown in this contribution were fully characterized by ¹H and ¹³C NMR spectroscopy, absorption and emission spectroscopy in dilute solutions and as thin films as well as by MALDI-TOF mass spec-

Table 1. Synthesis of the bis(terpyridines) T8-T16.^[a]

Code	Spacer	Linker	Yield [%]
Т8	ОЕН	double bond	79
T10		triple bond	77
T12	HEO	1,2,3 triazol-4-yl	54
Т9	ОЕН 🔿	double bond	87
T11		triple bond	72
T13	🔷 нео́	1,2,3 triazol-4-yl	44
T14		double bond	79
T15		triple bond	81
T16	C ₈ H ₁₇ C ₈ H ₁₇	1,2,3 triazol-4-yl	74

[a] Experimental details are given in the Supporting Information.

trometry. Additionally, several spacer and ligand systems were investigated by temperature-dependent absorption spectroscopy. Table 1 provides an overview of the synthesized systems, their spacer and linker units and the isolated yields.

Photophysical Properties

The photophysical properties of the π -conjugated terpyridines were investigated in detail by absorption and emission spectroscopy in solution (Table 2). In addition, we prepared thin films of the materials by spin-coating to study the optical properties in the solid state. Figure 2 shows the absorption and emission spectra of the phenyl-containing bis(terpyridines) T8, T10 and T12, connected to the spacer units through a double bond, triple bond and 1H-1,2,3-triazole, respectively, and illustrates the effect of the conjugated linker. As also summarized in Table 2, the longestwavelength absorption maximum shows a constant bathochromic shift of around 7 nm on going from the conjugated spacer unit without terpyridines (10, $\lambda_{abs} = 377$ nm) to the triazole-connected system (T12, $\lambda_{abs} = 384$ nm), the triple bond linked (T10, $\lambda_{abs} = 392$ nm) and the system containing the double bond (T8, $\lambda_{abs} = 399$ nm). The molar extinction coefficient increases in the same way. It has been proven by DFT calculations and experiments that a double bond next to a terpyridine unit leads to a higher degree of conjugation than in the case of a triple bond.^[40-42] This general trend can be verified by the experimental values reported herein. The fluorescence spectra show a strong $S_{10} \rightarrow S_{00}$ transition and a $S_{10} \rightarrow S_{01}$ transition as a shoulder. The emission maxima exhibit the same general trends as the absorption maxima.

Table 2. Selected photophysical properties of compounds 10, 11, 15 and T8–T16 in dilute solution $(10^{-6} \text{ M in CHCl}_3, 25 \text{ °C})$.

λ_{abs} [nm]	$\varepsilon [\mathrm{M}^{-1}\mathrm{cm}^{-1}]$	$\lambda_{\rm PL}$ [nm]	${\Phi_{ ext{PL}}}^{[a]}$
377	38000	418	0.70
399	100700	450	0.85
392	77400	438	0.75
384	56400	424	0.77
477	44200	500	0.73
478	99700	545	0.12
503	45400	553	0.25
482	51200	510	0.72
315	30800	330	0.24
399	98900	444	0.88
369	91200	404	0.77
328	89300	378	0.55
	$\begin{array}{c} \lambda_{abs} [nm] \\ 377 \\ 399 \\ 392 \\ 384 \\ 477 \\ 478 \\ 503 \\ 482 \\ 315 \\ 399 \\ 369 \\ 328 \\ \end{array}$	$\begin{array}{c c} \lambda_{abs} [nm] & \varepsilon [m^{-1} cm^{-1}] \\ \hline 377 & 38000 \\ 399 & 100700 \\ 392 & 77400 \\ 384 & 56400 \\ \hline 477 & 44200 \\ 478 & 99700 \\ 503 & 45400 \\ 482 & 51200 \\ \hline 315 & 30800 \\ 399 & 98900 \\ 369 & 91200 \\ 328 & 89300 \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

[a] Absolute fluorescence quantum yield.

Within this series, the quantum yield in solution is the highest for the double-bond-containing bis(terpyridine) **T8** ($\Phi_{PL} = 0.85$). Because no other structural parameters have been changed, the changes in optical properties can be unambiguously explained by the different linker units. The value of the absorption maximum is an indication of the conjugation length of the systems studied. Therefore, the surprisingly small bathochromic shift observed for **T12**



Figure 2. Normalized absorption and emission spectra of terpyridines **T8**, **T10** and **T12** and the spacer **10**. For all measurements: CHCl₃, 10^{-6} M, 25 °C.

compared with the spacer **10** can be explained by a nonoptimal conjugation through the 1*H*-1,2,3-triazole moiety. This assumption was confirmed by calculations and will be described in the Calculations section of this contribution in detail (see below). In the cases of **T10** and **T8**, the intensities of the longest wavelength bands also increase significantly compared with the one around $\lambda_{abs} = 320-350$ nm, which can be confirmed by the extinction coefficients (Table 2).

This trend can also be seen for the fluorene-containing bis(terpyridine) systems **T14–T16** (Figure 3, Table 2). In these systems no torsion is possible in the spacer unit itself and, therefore, all changes in the geometry have to occur in the connecting unit. Compared with the fluorene spacer unit (**15**), the longest-wavelength absorption maximum of the system connected by two triazole units (**T16**) is shifted by 13 nm. The introduction of a triple (**T15**, $\lambda_{abs} = 369$ nm, $\lambda_{PL} = 404$ nm) or a double bond (**T14**, $\lambda_{abs} = 399$ nm, $\lambda_{PL} = 444$ nm) leads to the expected redshift in the absorption and emission.



Figure 3. Normalized absorption and emission spectra of the spacer 15 and the bis(terpyridines) T14–T16. For all measurements: CHCl₃, 10^{-6} M, 25 °C.

When comparing the spectra of the anthracene-containing systems with each other, it is obvious that the spacer unit 11 ($\lambda_{abs} = 477$ nm), the triazole- (T13) ($\lambda_{abs} = 482$ nm) and double-bond- (T9) ($\lambda_{abs} = 478$ nm) -connected systems exhibit absorption maxima in the same region, but for different reasons. The connection of a triazole to the anthracene unit also leads, in addition to the electronic situation previously discussed for T12 and T16, to decreased conjugation due to steric hindrance. We have calculated that the interaction between the hydrogen atoms at the 1- and 8positions of the anthracene and the triazole leads to an energetic minimum at a dihedral angle of around 85°.

It has already been shown in the case of PPE/PPV-type polymers that a double bond connected to an anthracene unit at the 9- or 10-position leads to a torsion and, thereby, hindered conjugation in the ground state.^[43] This assumption was confirmed by analysing the emission spectra. Systems 11 ($\Delta v_{af} = 1000 \text{ cm}^{-1}$) and T13 ($\Delta v_{af} = 1100 \text{ cm}^{-1}$) exhibit small Stokes shifts, whereas **T9** ($\Delta v_{af} = 2600 \text{ cm}^{-1}$) shows a clearly larger shift as well as a remarkably low quantum yield and an unstructured emission band, which can be explained by the planarization of the conjugated system in the excited state and thus a large geometrical rearrangement. Consequently, steric effects are absent in the excited state, but electronic effects still hinder full conjugation in the case of T13. When the spacer unit is connected by triple bonds to the terpyridines (T11), the absorption is shifted to $\lambda_{abs} = 503$ nm as no steric or electronic effects hinder the conjugation in this case. As expected, the emission maximum appears in the same region as for T9 (Figure 4).



Figure 4. Normalized absorption and emission spectra of the spacer 11 and the bis(terpyridines) T9, T11 and T13. For all measurements: $CHCl_3$, 10^{-6} M, 25 °C.

The photophysical properties were also investigated in the solid state. In particular, the fluorene-containing bis(terpyridines) **T14–T16** were chosen because of their good solubility and film-forming properties. Thin films were prepared by spin-coating onto glass slides from solutions of 10 mg/ mL of the respective compound in chlorobenzene. The absorption and emission data obtained are summarized in Figure 5 and Table 3. A comparison of the data for dilute solutions and the solid state show that the absorption properties remain in principle the same: only small shifts of 220–460 cm⁻¹ were observed (Table 3). In contrast, the solid-state emission spectra exhibit large bathochromic shifts of 3725–5300 cm⁻¹ in comparison with the solution spectra. Additional shoulders are observed on the short-wavelength side of the luminescence bands, which exhibit energy differences of 740–830 cm⁻¹ compared with the solution emission maxima. Moreover, the photoluminescence quantum yields $\Phi_{\rm PL}$ show a notable decrease from 0.88, 0.77 and 0.55 in



Figure 5. UV/Vis absorption, emission and excitation spectra of a) **T14**, b) **T15** and c) **T16** in solution $(10^{-6} \text{ M in CHCl}_3, 25 \text{ °C})$ and as thin films.

solution to 0.14, 0.26 and 0.07 in the films, respectively. This behaviour can be explained by the formation of excimers (or larger aggregated excited species), as described in the literature.^[44] In this process an excited species forms a dimeric system with a non-excited one. Because excimers mostly possess cofacial sandwich-type configurations, the planar π -conjugated systems presented in this work are preeminently suited to form such species. Excimer formation leads to the appearance of an additional emission band that is both redshifted and unstructured (as can be observed in Figure 5) as well as to rapidly decreased photoluminescence quantum yields. The observed short-wavelength shoulders, which can be attributed to monomer emission, and the fact that excitation spectra with different emission wavelengths remain in principle constant support our assumption of excimer formation. In addition, the formation of excimers seems to be strongly dependent on film morphology; although different thin-film samples were prepared in the same way, they show slightly different intensity ratios between excimer and monomer emissions.

Table 3. Photophysical properties of compounds T14–T16 in dilute solution (10^{-6} M in CHCl₃, 25 °C) and as thin films.

	λ_{abs} [nm]		$\lambda_{\rm PL}$ [nm]		$\Phi_{ m PL}{}^{[a]}$	
	Solution	Film	Solution	Film ^[b]	Solution	Film
T14	397	401	442	532, 457s	0.88	0.14
T15	368	371	404	500, 418s	0.77	0.26
T16	327	332	378, 360	445, 390s, 371s	0.55	0.07

[a] Absolute fluorescence quantum yield. [b] s: short-wavelength shoulder.

Calculations

All the bis(terpyridines) described in this paper may be regarded as more or less conjugated multichromophoric π systems. The π conjugation may not extend over the entire molecule, but may be disturbed by torsional disorder and also by potential sinks within the chain. Standard quantum chemical calculations were performed in order to interpret the spectroscopic findings, to localize the essential chromophores and to identify rotational disorder. Density functional theory at the B3LYP/6-31g(d) level of theory was applied to all full geometry optimizations using the GAUSSIAN03 program package.^[45] For computational ease, the 2-ethylhexyloxy substituents and the octyl substituents in the fluorene-containing compounds were replaced by hydroxy groups and hydrogen atoms, respectively. Electronic transitions were calculated with the help of time-dependent density functional theory implemented in the same package. From an inspection of the frontier orbitals we may draw a series of qualitative conclusions, although the HOMO/LUMO configuration interaction (CI) coefficients for the S_1 state are only close to 0.66 throughout.

The π system of the terminal phenylterpyridine moiety is only negligibly involved in the frontier orbitals of **T10–T13**. The triazole units of **T12** and **T13** do not contribute to the frontier orbitals either (see also Figure 6).



Figure 6. Representation of the LUMO (top) and HOMO (bottom) of **T13**.

In other words, the chromophores of T12 and T13 can be identified as the spacer unit consisting of three arylenes linked by two ethynylene moieties. The same conclusion has to be drawn from a pairwise comparison of the absorption and emission spectra of the bis(terpyridine) with the corresponding spacer molecule (i.e., T12/8 and T13/9). With the vinylene-linked bis(terpyridines) T8 and T9, the HOMO extends well into the phenylene ring adjacent to the terpyridine and even the π orbitals of the middle pyridine rings are involved in the LUMO.^[46] This part of the π system is essentially flat in the case of T8. In T9, steric hindrance between the vinylene protons and two anthracene protons causes a tilt of about 70° between the planes of the anthracene and the phenylene moieties, as determined by structure optimization. Nevertheless, mediated by the vinylene moiety, conjugation also extends to the middle pyridine rings. The planes of the central part of the linker and the terpyridine are essentially perpendicular to each other. As a result of the larger size of the LUMO, one might expect some symmetric charge transfer from the centre of the molecules to the periphery. With the fluorene-containing bis(terpyridines) T14 and T15, the frontier orbitals include the phenylene rings attached to the middle pyridine ring. The π system is essentially flat and the triazole moieties in T16 do not interrupt the conjugation (Figure 7). The middle pyridine rings of T14 and T15 contribute significantly more to the LUMOs than to the HOMOs. Again, we can conclude that some symmetric charge transfer occurs from the centre of the molecules to the periphery upon excitation.

In addition, we recorded absorption spectra at low temperatures. The data have been interpreted by exemplarily comparing the calculated and experimental positions of the longest wavelength transitions of **T13** and its spacer unit **13**. When comparing the theoretical results ($\lambda_{max} = 551$ nm;



Figure 7. Representation of the LUMO (top) and HOMO (bottom) of T16.

oscillator strength of 1.362) with the experimental ones $(\lambda_{\max,20 \circ C} = 482 \text{ nm}, \lambda_{\max,-200 \circ C} = 502 \text{ nm})$, we have to take into consideration the fact that theory only predicts transitions for the ideal structure whereas the experiment at room temperature in solution gives an average ensemble of strongly torsionally disordered systems. Hence, the low-temperature spectra of samples with partially frozen tor-



Figure 8. Temperature-dependent absorption spectra of a) 13 and b) T13 10^{-5} to 10^{-6} M in 2-methyltetrahydrofuran.

sional motion compare significantly better with the computational model. An example of the thermochromism is presented in Figure 8. Furthermore, it is well known that DFT underestimates the energy difference between the S_1 and S_0 states for large extended π systems.^[47]

Because the temperature-dependent spectra of the spacer 13 and the corresponding bis(terpyridine) T13 are nearly the same we have to conclude that the torsional disorder is caused by the ethynylene links. The very different internal torsional barriers of 9-(triazol-4'-yl)anthracene and (triazol-4'-yl)benzene, calculated as 54 and 17.5 kJ/mol, respectively, apparently have only a negligible influence on the overall spectra. The spectral behaviour, including fluorescence, closely resembles the findings with arylene-ethynylene/arylene-vinylene copolymers and their low-molecular-mass model compounds, which have recently been reviewed.^[48]

Conclusions

In this contribution we have described the synthesis of a series of bis(terpyridines) containing phenyl, anthracene and fluorene systems. To be able to compare the results of a photophysical study of these compounds in detail we varied both the spacer unit as well as the connecting unit between the spacer and the terpyridine moiety in a systematic manner. In this way we found that 1H-1,2,3-triazole is invaluable for the connection of conjugated systems under mild conditions at room temperature. As a result of the non-optimal conjugation through this connecting unit, the resulting ligands exhibit the most hypsochromic-shifted absorption maxima. Through DFT calculations we have proven this explanation and also shown the fluorene system to be able to overlap with the p orbital of the tertiary nitrogen atom of the triazole and therefore extend the conjugation, which is also confirmed by the absorption spectra. A comparison of the absorption spectra of the systems studied herein with the same conjugated backbone shows the possibility of tuning the absorption maximum over a range of about 80 nm by just varying the connecting unit. In addition, the emission colour could easily be changed, which is an important consideration when aiming to synthesize ligands with potential applications as emitting layers in LED devices. The thin films of the ligands showed a very high tendency towards excimer formation and thus broad emission spectra and high Stokes shifts. Thus, this approach allows the synthesis of materials with tailor-made optical properties. Moreover, the corresponding metal complexes may be used for the construction of OLEDs and solar cells (for the first results of a study in this direction see, for example, ref.^[49]).

Experimental Section

Materials: All reagents were purchased from commercial sources and were used without further purification unless specified. Solvents were dried and distilled according to standard procedures. Unless otherwise specified, solvents or solutions were degassed by bubbling with argon 1 h prior to use. Compounds **2**, **7**, **14–18**, **T14** and **T15** were prepared following previously published protocols.^[17,27,43] All the terpyridine derivatives were purified by flash column chromatography (neutral alumina, CH₂Cl₂/MeOH as eluent) or preparative size-exclusion chromatography (BioBeads[®] S-X5, toluene as eluent). The commercially available boronic acids **5** and **6** were converted into the corresponding ethylene glycol boronate by heating with ethylene glycol at reflux in toluene.

Instrumentation: ¹H and ¹³C NMR spectra were obtained in deuterated chloroform at 25 °C using a Bruker DRX 400 or AC 250 instrument. UV/Vis absorption spectra were recorded in dilute CHCl₃ solutions with a Analytik Jena SPECORD 250 spectrometer. Emission spectra were measured with a Jasco FP-6500 spectrometer. Absolute quantum yields were determined by using a Hamamatsu C 10027 Photonic Multi-Channel Analyzer. UV/Vis absorption spectra of spin-coated films were obtained using a Perkin–Elmer UV/Vis/NIR Lambda 19 spectrometer; the emission data were recorded with a Hitachi F-4500 fluorescence spectrometer. MALDI-TOF mass spectra were obtained with an Ultraflex III TOF/TOF mass spectrometer with dithranol as matrix in reflector mode. Elemental analyses were carried out with a CHN-932 Automat Leco instrument.

Synthesis of the π -Conjugated Spacer Units by Sonogashira Reaction: The aryl halide 1, 2, 5 or 6 (6.3 mmol) was dissolved in a mixture of THF (20 mL) and diisopropylamine (10 mL). Cul (23 mg, 0.12 mmol) and [Pd(PPh_3)_4] (139 mg, 0.12 mmol) were added and the mixture was heated to 45 °C. A degassed solution of 7 (1.15 g, 3 mmol) in THF (10 mL) was added dropwise. The reaction mixture was stirred at 45 °C for 2–48 h. After cooling, the precipitate was removed by filtration. The solvent was then removed and the residue was redissolved in CHCl₃, washed with a sat. NH₄Cl solution and water, dried with MgSO₄ and the solution concentrated. In the case of aryl halides 4 and 5 a larger excess (15 mmol) was used to avoid polycondensation. Owing to their instability towards water, the spacer units 12 and 13 were not washed with water.

4,4'-{[2,5-Bis(2-Ethylhexyloxy)-1,4-phenylene]bis(ethynediyl)}dibenzaldehyde (8): The reaction of 4-bromobenzaldehyde (1; 1.17 g, 6.3 mmol) and 1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (7; 1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by column chromatography (silica gel, toluene/heptane, 5:1) and recrystallization from acetone to yield 8 as a yellow substance (1.31 g, 74%). ¹H NMR $(250 \text{ MHz}, \text{CDCl}_3): \delta = 10.02 \text{ (s, 2 H, CHO)}, 7.87 \text{ (AA', 4 H)}, 7.66$ (XX', 4 H), 7.04 (s, 2 H, C_{phenyl}-H), 3.94 (d, ${}^{3}J$ = 5.5 Hz, 2 H, OCH₂), 1.80 (m_c, ³J = 6.1 Hz, 2 H, CH), 1.67–1.23 (m, 16 H, CH₂), 0.99 (t, ${}^{3}J$ = 7.4 Hz, 6 H, ethyl-CH₃), 0.90 (t, ${}^{3}J$ = 6.9 Hz, 6 H, hexyl-CH₃) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 191.32 (CHO), 154.06 (C_{phenyl}-OR), 135.41, 131.96, 129.72, 129.57, 116.52, 113.84 (C_{phenyl}), 94.18, 90.12 (C≡C), 71.97 (OCH₂), 39.62 (CH), 30.87, 30.68, 29.14, 24.02, 23.05 (CH₂), 14.05 (ethyl-CH₃), 11.27 (hexyl-CH₃) ppm. MS (MALDI-TOF, dithranol): m/z =591.36 $[M + H]^+$. C₄₀H₄₆O₄ (590.79): calcd. C 81.32, H 7.85; found C 81.38, H 7.80.

10,10'-{[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis(ethynediyl)}dianthracene-9-carbaldehyde (9): The reaction of 9-bromoanthracene-10-carbaldehyde (2; 1.80 g, 6.3 mmol) and 7 (1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by column chromatography (silica gel, CHCl₃) to yield 9 a red substance (759 mg, 32%). ¹H NMR (400 MHz, CDCl₃): δ = 11.56 (s, 2 H, CHO), 8.97 (dd, 4 H), 7.73



(m_c, 4 H), 7.36 (s, 2 H, C_{phenyl}-H), 4.18 (d, ${}^{3}J$ = 5.6 Hz, 4 H, OCH₂), 2.03 (m_c, 2 H, CH), 1.80–1.26 (m, 16 H, CH₂), 1.02 (t, ${}^{3}J$ = 7.6 Hz, 6 H, ethyl-CH₃), 0.86 (t, ${}^{3}J$ = 6.8 Hz, 6 H, hexyl-CH₃) ppm. 13 C NMR (100 MHz, CDCl₃): δ = 192.94 (CHO), 154.29 (C_{phenyl}-OR), 131.92, 131.39, 128.99, 128.08, 126.58, 125.87, 125.25, 123.94, 116.26, 114.31 (C_{aryl}), 101.61, 92.30 (C=C), 71.97 (OCH₂), 39.69 (CH), 30.45, 29.12, 23.86, 23.03 (CH₂), 13.99 (ethyl-CH₃), 11.08 (hexyl-CH₃) ppm. MS (MALDI-TOF, dithranol): *m/z* = 791.43 [M + H]⁺. C₅₆H₅₄O₄ (791.03): calcd. C 85.03, H 6.88; found C 84.02, H 6.99.

4,4'-{[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis(ethynediyl)}bis(1iodobenzene) (10): The reaction of 1,4-diiodobenzene (3; 4.95 g, 15 mmol) and 7 (1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by column chromatography (silica gel, toluene/heptane, 2:1) and recrystallization from acetone to yield 10 as a yellow substance (708 mg, 30%). ¹H NMR (250 MHz, CDCl₃): δ = 7.69 (d, ³J = 8.3 Hz, 4 H), 7.23 (d, ${}^{3}J$ = 8.5 Hz, 4 H), 6.99 (s, 2 H), 3.90 (d, ${}^{3}J$ = 5.5 Hz, 4 H, OCH₂), 1.78 (m_c, 2 H, CH), 1.64–1.21 (m, 16 H, CH₂), 0.96 $(t, {}^{3}J = 7.3 \text{ Hz}, 6 \text{ H}, \text{ ethyl-CH}_{3}), 0.88 (t, {}^{3}J = 7.4 \text{ Hz}, 6 \text{ H}, \text{ hexyl-}$ CH₃) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 153.85 (C_{phenvl}-OR), 137.50, 132.95, 123.03, 116.47, 113.79, 94.04, 93.90, 87.47 (C_{arvl}, C≡C), 71.98 (OCH₂), 39.61 (CH), 30.66, 29.68, 29.14, 24.01, 23.05 (CH₂), 14.06 (ethyl-CH₃), 11.26 (hexyl-CH₃) ppm. MS (MALDI-TOF, dithranol): $m/z = 786.15 \text{ [M]}^+$. $C_{38}H_{44}I_2O_2$ (786.56): calcd. C 58.03, H 5.64, I 32.27; found C 59.03, H 5.98, I 31.56.

10,10'-{[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis(ethynediyl)}bis-(9-bromoanthracene) (11): The reaction of 9,10-dibromoanthracene (4; 5.04 g, 15 mmol) and 7 (1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by column chromatography (silica gel, CH₂Cl₂) to yield 11 as a red substance (616 mg, 23%). ¹H NMR (400 MHz, CDCl₃): δ = 8.87 (m_c, 4 H), 8.62 (m_c, 4 H), 7.70–7.64 (m, 8 H), 7.34 (s, 2 H), 4.17– 4.13 (m, 4 H, OCH₂), 2.00 (m_c, 2 H, CH), 1.78-1.28 (m, 16 H, CH₂), 1.01 (t, ${}^{3}J$ = 7.6 Hz, 6 H, ethyl-CH₃), 0.85 (t, ${}^{3}J$ = 7.2 Hz, 6 H, hexyl-CH₃) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 153.97 (C_{phenvl}-OR), 132.98, 130.34, 128.20, 127.62, 127.45, 126.71, 124.16, 118.66, 116.05, 114.14 (C_{aryl}), 98.84, 91.84 (C=C), 71.83 (OCH₂), 39.67 (CH), 30.42, 29.68, 29.11, 23.82, 23.04 (CH₂), 14.02 (ethyl-CH₃), 11.07 (hexyl-CH₃) ppm. MS (MALDI-TOF, dithranol): $m/z = 890.24 [M]^+$. $C_{54}H_{52}Br_2O_2$ (892.80): calcd. C 72.65, H 5.87, Br 17.90; found C 72.87, H 6.06, Br 17.54.

2,2'-{4,4'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis(ethynediyl)bis(4,1-phenylene)}di-1,3,2-dioxaborolane (12): The reaction of 2-(4iodophenyl)-1,3,2-dioxaborolane (5; 1.73 g, 6.3 mmol) and 7 (1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by recrystallization from THF to yield 12 as a yellow substance (1.62 g, 79%). ¹H NMR (250 MHz, CDCl₃): δ = 7.80 (d, ³J = 8.0 Hz, 4 H), 7.54 (d, ³J = 7.5 Hz, 4 H), 7.02 (s, 2 H), 4.39 [s, 8 H, B(OCH₂)₂], 3.92 (d, ${}^{3}J$ = 5.8 Hz, 4 H, OCH₂), 1.80 (m_c, 2 H, CH), 1.67–1.26 (m, 16 H, CH₂), 0.97 (t, ${}^{3}J = 7.5$ Hz, 6 H, ethyl-CH₃), 0.88 (t, ${}^{3}J = 7.3$ Hz, 6 H, hexyl-CH₃) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 153.90 (C_{phenyl}-OR), 134.64, 130.81, 126.48, 116.60, 113.91 (C_{arvl}), 94.86, 87.63 (C=C), 72.05 (OCH₂), 66.12 [(OCH₂)₂], 39.65 (CH), 30.68, 29.17, 24.01, 23.08 (CH₂), 14.09 (ethyl-CH₃), 11.29 (hexyl-CH₃) ppm. C₄₂H₅₂B₂O₆ (674.48): calcd. C 74.79, H 7.77; found C 75.12, H 7.97.

2,2'-{10,10'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis(ethynediyl)-bis(anthracene-10,9-diyl)}di-1,3,2-dioxaborolane (13): The reaction of 2-(10-bromoanthracen-9-yl)-1,3,2-dioxaborolane (**6**; 2.06 g,

6.3 mmol) and 7 (1.15 g, 3 mmol) was carried out according to the general procedure. The crude product was purified by recrystallization from toluene to yield **13** as a red substance (2.13 g, 81%). ¹H NMR (250 MHz, CDCl₃): $\delta = 8.80$ (d, ³*J* = 7.8 Hz, 4 H), 8.33 (d, ³*J* = 7.3 Hz, 4 H), 7.66–7.54 (m, 8 H), 7.34 (s, 2 H), 4.68 [s, 8 H, B(OCH₂)₂], 4.15 (d, ³*J* = 5.38 Hz, 4 H, OCH₂), 2.02 (m_c, 2 H, CH), 1.80–1.22 (m, 16 H, CH₂), 1.00 (t, ³*J* = 7.5 Hz, 6 H, ethyl-CH₃), 0.85 (t, ³*J* = 7.0 Hz, 6 H, hexyl-CH₃) ppm. ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 153.98$ (C_{phenyl}-OR), 135.32, 131.87, 129.01, 127.66, 126.10, 126.03, 120.66, 116.16, 114.20 (C_{aryl}), 98.86, 92.36 (C=C), 71.84 (OCH₂), 66.27 [(OCH₂)₂], 39.66 (CH), 30.42, 29.11, 23.82, 23.05 (CH₂), 14.04 (ethyl-CH₃), 11.08 (hexyl-CH₃) ppm. C₅₈H₆₀B₂O₆ (874.72): calcd. C 79.64, H 6.91; found C 79.92, H 7.12.

Synthesis of Bis(terpyridines) by Horner–Wadsworth–Emmons (HWE) Reaction: KOtBu (34 mg, 0.3 mmol) was added to a solution of a dialdehyde 8, 9 or 14 (0.2 mmol) and 18 (184 mg, 0.4 mmol) in toluene (20 mL). The reaction mixture was heated at reflux for 3 h and subsequently quenched with an aq. 10% HCl solution (10 mL). The organic phase was separated and washed with distilled water. The organic phase was dried with MgSO₄ and then evaporated. The crude product was purified as described above.

4,4'-(4,4'-(1E,1'E)-2,2'-{4,4'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylenelbis(ethynediyl)bis(4,1-phenylene)}bis(ethene-2,1-diyl)bis(4,1phenylene))bis(2,2':6',2''-terpyridin-4-yl) (T8): The reaction of 8 (118 mg, 0.2 mmol) and diethyl 4-(2,2':6',2''-terpyridin-4'-yl)benzylphosphonate (18; 184 mg, 0.4 mmol) was carried out according to the general procedure for the HWE reaction. After purification T8 was obtained as a yellow substance (192 mg, 79%). ¹H NMR (400 MHz, CDCl₃): δ = 8.78 (s, 4 H, tpy-H^{3',5'}), 8.75 (d, ³J = 5.0 Hz, 4 H, tpy-H^{3,3''}), 8.69 (d, ${}^{3}J$ = 8.0 Hz, 4 H, tpy-H^{6,6''}), 7.95 (AA', 4 H), 7.90 (t, ${}^{3}J$ = 7.8 Hz, 4 H, tpy-H^{4,4''}), 7.66 (XX', 4 H), 7.54 (AA'XX', 4 H), 7.38 (t, ${}^{3}J$ = 5.2 Hz, 4 H, tpy-H^{5,5''}), 7.21 (s, 4 H), 7.04 (s, 2 H, C_{phenyl}-H), 3.95 (d, ${}^{3}J = 5.5$ Hz, 4 H, OCH₂), 1.84 (m_c, 2 H, CH), 1.73–1.22 (m, 16 H, CH₂), 1.01 (t, ${}^{3}J$ = 7.3 Hz, 6 H, ethyl-CH₃), 0.92 (t, ${}^{3}J$ = 6.8 Hz, 6 H, hexyl-CH₃) ppm. ${}^{13}C$ NMR (100 MHz, CDCl₃): δ = 154.30, 156.00, 153.92, 149.63, 149.13, 137.95, 137.70, 137.07, 136.87, 131.89, 128.88, 128.84, 127.65, 127.14, 126.54, 123.82, 122.84, 121.40, 118.57, 116.63, 114.03 (C_{phenvl}), 95.07, 87.32 (C=C), 72.12 (OCH₂), 39.71 (CH), 30.72, 29.21, 24.07, 23.09 (CH₂), 14.09 (ethyl-CH₃), 11.31 (hexyl-CH₃) ppm. MS (MALDI-TOF, dithranol): m/z = 1201.62 [M + H]⁺. C₈₄H₇₆N₆O₂ (1201.54): calcd. C 83.97, H 6.38, N 6.99; found C 84.21, H 6.52, N 6.73.

4,4'-(4,4'-(1E,1'E)-2,2'-{10,10'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene|bis(ethynediyl)bis(anthracene-10,9-diyl)}bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(2,2':6',2''-terpyridin-4-yl) (T9): The reaction of 9 (158 mg, 0.2 mmol) and 18 (184 mg, 0.4 mmol) was carried out according to the general procedure for the HWE reaction. After purification T9 was obtained as an orange substance (238 mg, 87%). ¹H NMR (300 MHz, CDCl₃): δ = 8.92 (d, ³J = 8.6 Hz, 4 H, C_{anth} -H), 8.84 (s, 4 H, tpy-H^{3',5'}), 8.78 (d, ³J = 5.4 Hz, 4 H, tpy- $H^{3,3''}$), 8.72 (d, ${}^{3}J$ = 8.1 Hz, 4 H, $H^{6,6''}$), 8.46 (m, 4 H, C_{anth}-H), 8.10–8.01 (m, AA', CH=CH, 6 H), 7.92 (t, ${}^{3}J$ = 7.6 Hz, 4 H, tpy- $H^{4,4''}$), 7.83 (XX', 4 H), 7.70–7.52 (m, C_{anth}-H, 8 H), 7.40 (t, ${}^{3}J$ = 5.42 Hz, 4 H, tpy-H^{5,5''}), 7.33 (s, 2 H, C_{phenyl}-H), 7.07 (d, ${}^{3}J$ = 16.5 Hz, 2 H), 4.16 (d, ${}^{3}J$ = 5.6 Hz, 4 H, OCH₂), 2.05 (m_c, ${}^{3}J$ = 6.2 Hz, 2 H, CH), 1.83–1.26 (m, 16 H, CH₂), 1.03 (t, ${}^{3}J$ = 7.2 Hz, 6 H, ethyl-CH₃), 0.87 (t, ${}^{3}J$ = 6.9 Hz, 6 H, hexyl-CH₃) ppm. The ¹³C NMR spectrum could not be measured due to the low solubility of **T9**. MS (MALDI-TOF, dithranol): m/z = 1402.75 [M +

H]⁺. C $_{100}$ H $_{84}$ N $_{6}$ O $_{2}$ (1401.78): calcd. C 85.68, H 6.04, N 6.00; found C 85.92, H 6.32, N 5.82.

Synthesis of Bis(terpyridines) by Sonogashira Reaction: CuI (6 mg, 0.032 mmol) and $[Pd(PPh_3)_4]$ (18 mg, 0.016 mmol) were added to a solution of the dihalide derivative **10**, **11** or **15** (0.2 mmol) and **17** (133 mg, 0.4 mmol) in a mixture of THF (5 mL) and diisopropylamine (2 mL) and the mixture was stirred at 45 °C for 24 h. After cooling, the precipitate was removed by filtration. The solvent was removed and the residue was redissolved in CHCl₃, washed with a sat. NH₄Cl solution and water, dried with MgSO₄ and concentrated. The crude product was purified as described above.

4,4'-(4,4'-{4,4'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis(ethynedil)bis(4,1-phenylene)}bis(ethynediyl)bis(4,1-phenylene))bis-(2,2':6',2''-terpyridin-4-yl) (T10): The reaction of 10 (157 mg, 0.2 mmol) and 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (17; 133 mg, 0.4 mmol) was carried out according to the general procedure for the Sonogashira reaction. After purification T10 was obtained as an orange substance (180 mg, 77%). ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (s, 4 H, tpy-H^{3',5'}), 8.67 (d, ³J = 4.8 Hz, 4 H, tpy-H^{3,3''}), 8.60 (d, ${}^{3}J$ = 8.0 Hz, 4 H, tpy-H^{6,6''}), 7.85 (AA', 4 H), 7.81 (t, ${}^{3}J = 7.6 Hz, 4 H, tpy-H^{4,4''}), 7.60 (XX', 4 H),$ 7.46 (AA'XX', 8 H), 7.29 (t, ${}^{3}J$ = 6.0 Hz, 4 H, tpy-H^{5,5''}) 7.00 (s, 2 H, C_{phenvl}-H), 3.87 (d, ${}^{3}J$ = 5.6 Hz, 4 H, OCH₂), 1.75 (m_c, 2 H, CH), 1.60–1.21 (m, 16 H, CH₂), 0.92 (t, ${}^{3}J$ = 7.6 Hz, 6 H, ethyl-CH₃), 0.84 (t, ${}^{3}J$ = 7.2 Hz, 6 H, hexyl-CH₃) ppm. ${}^{13}C$ NMR $(100 \text{ MHz}, \text{CDCl}_3)$: $\delta = 156.18, 156.11, 153.96, 149.35, 149.16,$ 138.40, 136.87, 132.18, 131.59, 131.48, 127.31, 123.88, 123.86, 123.58, 122.90, 121.37, 118.68, 116.62, 113.97 (C_{phenyl}), 94.65, 91.03, 90.67, 88.18 (C=C), 72.12 (OCH₂), 39.69 (CH), 30.72, 29.20, 24.06, 23.09 (CH₂), 14.08 (ethyl-CH₃), 11.30 (hexyl-CH₃) ppm. MS (MALDI-TOF, dithranol): $m/z = 1198.59 [M + H]^+$. $C_{84}H_{72}N_6O_2$ (1197.51): calcd. C 84.25, H 6.06, N 7.02; found C 84.42, H 6.29, N 6.69.

4,4'-(4,4'-{10,10'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis(ethynediyl)bis(anthracene-10,9-diyl)}bis(ethynediyl)bis(4,1-phenylene))bis(2,2':6',2''-terpyridin-4-yl) (T11): The reaction of 11 (179 mg, 0.2 mmol) and 17 (133 mg, 0.4 mmol) was carried out according to the general procedure for the Sonogashira reaction. After purification T11 was obtained as a red substance (196 mg, 72%). ¹H NMR (400 MHz, CDC1₃): \delta = 8.90–8.69 (m, 20 H), 7.97 (AA'XX', 8 H), 7.91 (t, ³J = 7.5 Hz, 4 H, tpy-H^{4,4''}) 7.76–7.65 (m, 8 H), 7.39 (t, ³J = 5.9 Hz, 4 H, tpy-H^{5,5''}) 7.32 (s, 2 H, C_{phenyl}-H), 4.16 (d, ³J = 5.3 Hz, 4 H, OCH₂), 2.04 (m_c, 2 H, CH), 1.84–1.22 (m, 16 H, CH₂), 1.03 (t, ³J = 7.5 Hz, 6 H, ethyl-CH₃), 0.87 (t, ³J = 7.0 Hz, 6 H, hexyl-CH₃) ppm. The ¹³C NMR spectrum could not be measured due to the low solubility of T11. MS (MALDI-TOF, dithranol): m/z = 1398.68 [M + H]⁺. C₁₀₀H₈₀N₆O₂ (1397.74): calcd. C 85.93, H 5.77, N 6.01; found C 86.21, H 6.02, N 5.82.

Synthesis of Bis(terpyridines) by "Click" Reaction: NaN₃ (32 mg, 0.5 mmol) and anhydrous CuSO₄ (16 mg, 0.1 mmol) were suspended in MeOH (2 mL). Subsequently, the aromatic glycol boronate **12**, **13** or **16** (0.2 mmol) was added. The mixture was stirred vigorously at room temperature until full conversion of the boronic acid ester (TLC monitoring). Subsequently, H₂O (0.1 mL), ethanol (2 mL), sodium ascorbate (4 mg, 0.02 mmol), CuI (38 mg, 0.2 mmol) and **18** (133 mg, 0.4 mmol) were added. The resulting mixture was heated under microwave irradiation at 100 °C for 1 h. After cooling, H₂O (15 mL) was added and the precipitate was collected by filtration. The precipitate was washed with *N*-(2-hydroxy-ethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid (HEDTA) solution (10 mL) and water. The residue was extracted with toluene and the



solution was dried with $MgSO_4$ and then evaporated. The crude product was purified as mentioned above.

4,4'-[4,4'-(1,1'-{4,4'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis-(ethynediyl)bis(4,1-phenylene)}bis[1H-[1,2,3]-triazole-4,1-diyl])**bis(4,1-phenylene)[bis(2,2':6',2''-terpyridine) (T12):** The reaction of 12 (135 mg, 0.2 mmol) and 17 (133 mg, 0.4 mmol) was carried out according to the general procedure for the "click" reaction. After purification T12 was obtained as a white substance (139 mg, 54%). ¹H NMR (400 MHz, CDCl₃): δ = 8.76 (s, 4 H, tpy-H^{3',5'}), 8.70 (d, ${}^{3}J = 5.4$ Hz, 4 H, tpy-H ${}^{3,3''}$), 8.62 (d, ${}^{3}J = 8.2$ Hz, 4 H, tpy-H ${}^{6,6''}$), 8.20 (s, 2 H), 7.99 (AA'XX', 8 H), 7.82 (t, ${}^{3}J$ = 7.5 Hz, 4 H, tpy- $H^{4,4''}$), 7.77 (AA', 4 H), 7.65 (XX', 4 H), 7.29 (t, ${}^{3}J$ = 4.8 Hz, 4 H, tpy-H $^{5,5^{\prime\prime}}),\,7.01$ (s, 2 H, C $_{phenyl}\text{-}H),\,3.93$ (m $_c,\,4$ H, OCH $_2),\,1.79$ (m $_c,\,$ 2 H CH), 1.65–1.27 (m, 16 H, CH₂), 0.97 (t, ${}^{3}J$ = 7.8 Hz, 6 H, ethyl-CH₃), 0.88 (t, ${}^{3}J$ = 7.2 Hz, 6 H, hexyl-CH₃) ppm. ${}^{13}C$ NMR $(100 \text{ MHz}, \text{CDCl}_3)$: $\delta = 156.46, 156.22, 154.24, 149.60, 149.12,$ 148.12, 138.75, 136.63, 136.45, 132.85, 130.90, 127.87, 126.42, 124.41, 123.63, 121.31, 120.29, 118.73, 117.46, 117.09, 114.23 (C_{arvl}), 93.60, 88.31, (C≡C), 72.54 (OCH₂), 39.89 (CH), 30.79, 29.20, 24.18, 22.97 (CH₂), 13.85 (ethyl-CH₃), 11.19 (hexyl-CH₃) ppm. MS (MALDI-TOF, dithranol): m/z = 1283.67 [M + H]⁺. C₈₄H₇₄N₁₂O₂ (1283.57): calcd. C 78.60, H 5.81, N 13.09; found C 78.84, H 6.09, N 13.01.

4,4'-[4,4'-(1,1'-{10,10'-[2,5-Bis(2-ethylhexyloxy)-1,4-phenylene]bis-(ethynediyl)bis(anthracene-10,9-diyl)}bis[1H-[1,2,3]triazole-4,1-diyl])bis(4,1-phenylene)]bis(2,2':6',2''-terpyridin-4-yl) (T13): The reaction of 13 (175 mg, 0.2 mmol) and 17 (133 mg, 0.4 mmol) was carried out according to the general procedure for the "click" reaction. After purification T13 was obtained as an off-white substance (131 mg, 44%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.92$ (d, ³J = 8.8 Hz, 4 H) 8.81 (s, 4 H, tpy-H^{3',5'}), 8.74 (d, ${}^{3}J$ = 4.4 Hz, 4 H, tpy- $H^{3,3''}$), 8.67 (d, ${}^{3}J$ = 8.0 Hz, 4 H, tpy- $H^{6,6''}$), 8.30 (s, 2 H), 8.07 (AA'XX', 8 H), 7.87 (t, ${}^{3}J$ = 7.5 Hz, 4 H, tpy-H^{4,4''}), 7.68 (t, ${}^{3}J$ = 8.0 Hz, 4 H), 7.59 (t, ${}^{3}J$ = 6.4 Hz, 4 H), 7.47–7.44 (m, 4 H), 7.34 (t, ${}^{3}J$ = 6.2 Hz, 4 H, tpy-H^{5,5''}) 7.28 (s, 2 H, C_{phenyl}-H), 4.12 (d, ${}^{3}J$ = 5.8 Hz, 4 H, OCH₂), 2.00 (m_c, 2 H, CH), 1.81-1.22 (m, 16 H, CH₂), 1.01 (t, ${}^{3}J$ = 7.8 Hz, 6 H, ethyl-CH₃), 0.85 (t, ${}^{3}J$ = 7.2 Hz, 6 H, hexyl-CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 156.29, 156.13, 154.15, 149.54, 149.16, 147.40, 138.44, 136.86, 132.18, 130.94, 128.67, 128.29, 128.18, 127.91, 127.51, 126.99, 126.44, 124.56, 123.85, 122.64, 121.68, 121.41, 118.67, 116.22, 114.20 (C_{arvl}) , 99.97, 91.56 (C=C), 72.04 (OCH₂), 39.78 (CH), 30.51, 29.18, 23.93, 23.09 (CH₂), 14.05 (ethyl-CH₃), 11.13 (hexyl-CH₃) ppm. MS (MALDI-TOF, dithranol): m/z = 1483.74 [M + H]⁺. C₁₀₀H₈₂N₁₂O₂ (1483.80): calcd. C 80.95, H 5.57, N 11.33; found C 81.18, H 5.64, N 10.89.

4,4'-(4,4'-(1,1'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(1H-[1,2,3]-triazole-4,1-diyl))bis(4,1-phenylene))bis(2,2':6',2''-terpyridin-4-yl) (T16): The reaction of 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)di-1,3,2-dioxaborolane (16; 106 mg, 0.2 mmol) and 17 (133 mg, 0.4 mmol) was carried out according to the general procedure for the "click" reaction. After purification T16 was obtained as a white substance (169 mg, 74%). ¹H NMR (400 MHz, CDCl₃): δ = 8.82 (s, 4 H, tpy-H^{3',5'}), 8.77 (d, ${}^{3}J$ = 3.6 Hz, 4 H, tpy-H^{3,3''}), 8.70 (d, ${}^{3}J = 8.0$ Hz, 4 H, tpy-H^{6,6''}), 8.38 (s, 2 H), 8.08 (AA'XX', 8 H), 7.92–7.80 (m, 10 H), 7.38 (t, ${}^{3}J$ = 6.0 Hz, 4 H, tpy-H^{5,5''}) 2.15 (m_c, 4 H, CH₂), 1.20–0.99 (m, 20 H, CH₂), 0.80 (t, ${}^{3}J$ = 7.2 Hz, 6 H, CH₃), 0.77–0.69 (m, 4 H, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 156.22, 156.06, 153.06, 149.58, 149.18, 147.96, 140.39, 138.40, 136.94, 136.57, 130.95, 127.92, 126.38, 123.94, 121.43, 121.20, 119.57, 118.66, 118.06, 115.31 (Carvl), 56.33, 40.36, 31.77, 29.96, 29.30, 29.24, 23.94, 22.60, 14.09 ppm. MS (MALDI-TOF,

dithranol): $m/z = 1139.55 [M + H]^+$. C₇₅H₇₀N₁₂ (1139.44): calcd. C 79.06, H 6.19, N 14.75; found C 79.08, H 6.18, N 14.70.

Supporting Information (see also the footnote on the first page of this article): ¹H NMR and MALDI-TOF MS spectra of the bis(terpyridines) **T8–T16**.

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