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Synthesis of Rigid π-Conjugated Mono-, Bis-, Tris-, and Tetrakis(terpyridine)s: Influence of the Degree and Pattern of Substitution on the Photophysical Properties

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A series of rigid π-conjugated mono-, bis-, tris-, and tetrakis(terpyridine)s **3**–**8** was synthesized in high yields by means of Horner–Wadsworth–Emmons (HWE) reactions between benzyl phosphonates **1** and an aldehyde-functionalized terpyridine derivative **2**. The photophysical properties of the materials in solution and in the solid state depend strongly both on the numbers of terpyridine moieties attached to the central phenyl cores and on the geometries of the compounds. The photophysical behavior of the *ortho*-substituted compounds **5** and **8** indicated significant changes in the geometries, together with major extensions of the effective π-conjugated systems upon excitation. Bright green emission with high quantum yields was observed for the tetrakis(terpyridine) derivative **8**.

Introduction

The self-assembly of functional structures into metallo-supramolecular architectures through the interaction of transition metal ions and appropriate ligands is a highly active area in modern supramolecular chemistry. The characteristics of these interactions are defined by combinations of various parameters, including the coordination numbers, geometries, and donor-types of the transition metal ions, and the numbers, types, and arrangements of the donor atoms of the ligands.[1]

In addition to the intensively elaborated N-heterocyclic systems based on 2,2′-bipyridine[2] and 1,10-phenanthroline,[3] 2,2′:6′,2′′-terpyridine derivatives have in recent years attracted much interest as versatile templates in supramolecular and coordination chemistry, as well as in materials science.[1,4–5] Their rich coordination chemistry and remarkably high binding affinities towards most transition metal ions, through dπ→pπ* bonding, make them highly attractive building blocks for the construction of complex metallo-supramolecular architectures with advanced photophysical, electrochemical, catalytic, and magnetic properties.[1] These properties can be influenced and tuned by variation of π-conjugated substituents attached at the 4′-position of the 2,2′:6′,2′′-terpyridine moiety.[5–6] Thanks to their electro-optical properties, the development of efficient and straightforward routes to tailor-made 2,2′:6′,2′′-terpyridines is a focus of current research.[7] It has been demonstrated that appropriate combinations of such chelating terpyridines and transition metal ions enable the synthesis of complexes featuring interesting luminescent properties. These structures are thus important candidates as hosts for photoinduced energy- and electron-transfer processes in the field of supramolecular chemistry.[6]

Furthermore, oligo(terpyridine)s are also used for the construction of supramolecular metallo-polymers. The electronic communication between the metal-complexed moieties within these structures is another aspect that highlights their potential in the design of new functional materials,[1,5–6] and a large number of studies on the construction of linear-rod polymers based on such conjugated oligo(terpyridine) moieties through the use of heavy transition metal ions – such as ruthenium(II), iridium(III) or osmium(II) – have been published.[8] Zinc(II) ions have also recently attracted much interest as novel templates for the fabrication of structurally well defined photoluminescent and electroluminescent supramolecular metallo-cycles and metallo-polymers.[9]

The photophysical properties of oligo(terpyridine)s and their transition metal complexes can be easily controlled through the electronic properties of the π-conjugated linkages. So far, only a few publications have dealt with the synthesis and properties of such rigid-linear or even star-shaped derivatives.[10] We have previously reported on the synthesis and characterization of a library of soluble rigid-linear π-conjugated bis(terpyridine)s.[10a] Those compounds

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exhibited bright emissions in the blue range ($\lambda_{PL,max}$ = 440–490 nm), with high quantum yields (Φ_{PL}) of up to 0.85 in dilute solutions. Variation in the conjugated system – including alkene, alkyne, and (hetero)aromatic moieties – was achieved through combinations of Pd^0-catalyzed coupling reactions and the Horner–Wadsworth–Emmons (HWE) reaction.

Here we describe a general protocol for the effective synthesis of mono(terpyridine)s, rigid-linear and -angular bis(terpyridine)s, and star-shaped tris- and tetrakis(terpyridine)s based on the same π-conjugated backbone. The influences of the substitution pattern and the number of terpyridine units attached to a central phenyl core on the photophysical properties in solution and in the solid state are also investigated in detail. The described oligo(terpyridine)s should in future work serve as templates for self-assembly with suitable transition metal ions to form linear and crosslinked metallo-polymers for potential optoelectronic applications.

Results and Discussion

Synthesis and Characterization

For our investigations we chose a system based on benzene as the central core with the terpyridine units attached to this through C=C links; the target compounds are summarized in Scheme 1. The alkoxy chains (i.e., *n*-octyloxy groups) were introduced to assure good solubility of the rigid terpyridine structures in common organic solvents. Because their yields are significantly higher than those of Pd^0-catalyzed coupling reactions and their starting materials are easily accessible, Wittig-type condensation reactions have been found to be the methods of choice for the attachment of π-conjugated building blocks to the terpyridine moieties.[9a] A general synthetic approach in which a previously introduced aldehyde-functionalized mono(terpyridine)[10a] is prepared and subsequently treated with an appropriate benzylic phosphonate **1** was therefore selected (Scheme 1).

The Michaelis–Arbusov reaction was used for the preparation of the benzylic phosphonates **1**.[11] The phosphonates **1a**–**f** were synthesized from the corresponding starting benzyl bromides by the general protocol in very high yields (≥90%; Scheme 2, Table 1). The reactions were carried out neat under inert conditions with excess triethylphosphite as both reactant and solvent (12 h, 120 °C). The structures of the phosphonates were confirmed by NMR spectroscopy and mass spectrometry. The ^{31}P NMR spectra of compounds **1** recorded in $CDCl_3$ in each case showed the characteristic singlet with the expected chemical shift in the range of 26–27 ppm.[12]

As shown previously, Sonogashira cross-coupling between 4′-(4-ethynylphenyl)-2,2′:6′,2′′-terpyridine and 4-bromo-2,5-bis(octyloxy)benzaldehyde in the presence of $Pd(PPh_3)_4$/CuI as catalytic system can directly result in the aldehyde-functionalized mono(terpyridine) **2** in good yield (52%; Scheme 3).[10a]

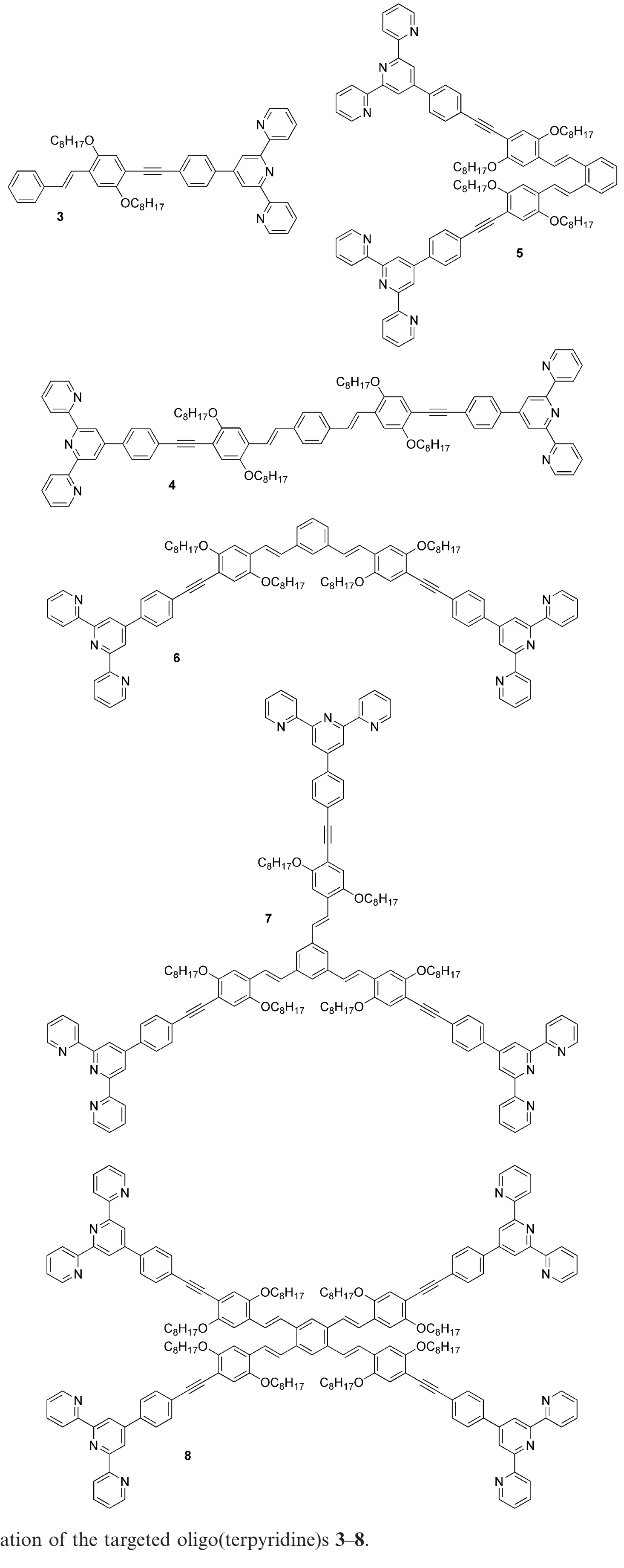
The HWE reaction has been found to represent a powerful tool for the straightforward synthesis of rigid π-conjugated bis(terpyridine)s.[10a,10b] In continuation of previous work, we have now coupled a series of benzylic phosphonates (**1**) with the aldehyde derivative **2** in the appropriate stoichiometry in the presence of KO^{t}Bu as base (Scheme 3). All oligo(terpyridine)s **3**–**8** were isolated in yields higher than 75% after column chromatography and subsequent precipitation into methanol. The efficiency of the HWE reaction is demonstrated by the fact that no major decreases in the obtained yields were observed for the sterically hindered *ortho*-substituted compounds **5** and **8**. The results of the HWE reactions are summarized in Table 2. All synthesized terpyridine derivatives have been fully characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. As shown by ^{1}H NMR spectroscopy (Figure 1), the formation of the C=C bonds occurred with very high *E* selectivity ($^3J_{H,H}$ = 15–17 Hz for the *E* configuration). The *Z* isomers were not detected spectroscopically. In all cases the NMR spectra showed well resolved signals; this indicates that aggregation of the highly conjugated systems through π–π stacking is generally prevented.

Since the film-forming abilities of rigid (unsubstituted) terpyridines are often very poor, only a few publications have dealt with the solid-state properties of these compounds.[9a] As expected, though, thanks to the attached alkoxy chains used here, improved solubilities in organic solvents of medium polarity relative to analogous structures known from the literature have been achieved. Furthermore, we have obtained homogeneous and transparent films by spin-coating the linear bis(terpyridine) **4** and the star-shaped systems **7** and **8** from $CHCl_3$ solutions onto glass slides. The film thicknesses have been determined to be in the range of 50 nm. As expected, the film-forming ability of the one-armed derivative **3** is very low. In the cases of **5** and **6** we were also unable to obtain homogeneous films, and so these materials could not be investigated further in the solid state.

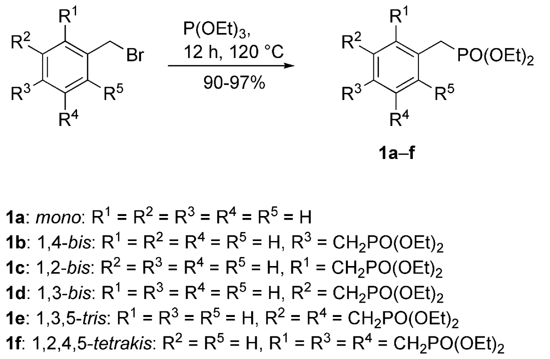
Photophysical Properties

The photophysical properties of the π-conjugated oligo(terpyridine)s **3**–**8** were investigated by absorption and photoluminescence (PL) spectroscopy both in dilute solution and in the solid state.

As illustrated in Figure 2 (top), the absorption spectra of **3**–**8** in dilute $CHCl_3$ solutions are in general each characterized by two intense bands. The band around 300 nm has been assigned to the characteristic π→π* transitions of the terpyridine moieties, whereas the broad band in the visible region (375–425 nm; Table 3) corresponds to π→π* transitions based on the overall π-conjugated system.[10a] For the mono(terpyridine) **3** this absorption maximum was found at 380 nm. With increasing numbers of π-conjugated terpyridine moieties on the central phenyl core, significant red shifts of the absorption maximum are observed, together with increases in the molar extinction coefficient. As would



Scheme 1. Schematic representation of the targeted oligo(terpyridine)s **3**–**8**.



Scheme 2. Schematic representation of the synthesis of the benzylic phosphonates **1a**–**f**.

Table 1. Synthesis of the benzylic phosphonates **1**.

Entry	Substitution pattern	Yield (%)	^{31}P NMR[c] δ_P (ppm)
1a	mono	92[a]	26.40
1b	1,4-bis	97[b]	26.25
1c	1,2-bis	90[a]	26.75
1d	1,3-bis	93[b]	26.26
1e	1,3,5-tris	95[b]	26.03
1f	1,2,4,5-tetrakis	96[b]	26.39

[a] Isolated yield after kugelrohr distillation. [b] Isolated yield after precipitation from hexane. [c] Measured in CDCl$_3$ (400 MHz, room temperature).

Table 2. Overview of the HWE reactions between the benzylic phosphonates **1** and the aldehyde-functionalized terpyridine **2**.

Entry	Substitution pattern	Yield [%][a]
3	mono	92
4	1,4-bis	88
5	1,2-bis	79
6	1,3-bis	83
7	1,3,5-tris	81
8	1,2,4,5-tetrakis	75

[a] Isolated yield after column chromatography and precipitation into methanol.

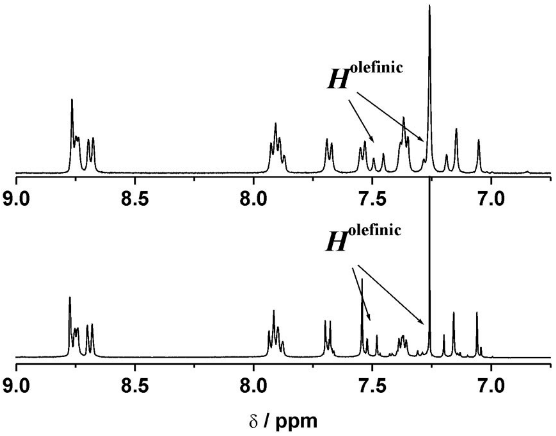
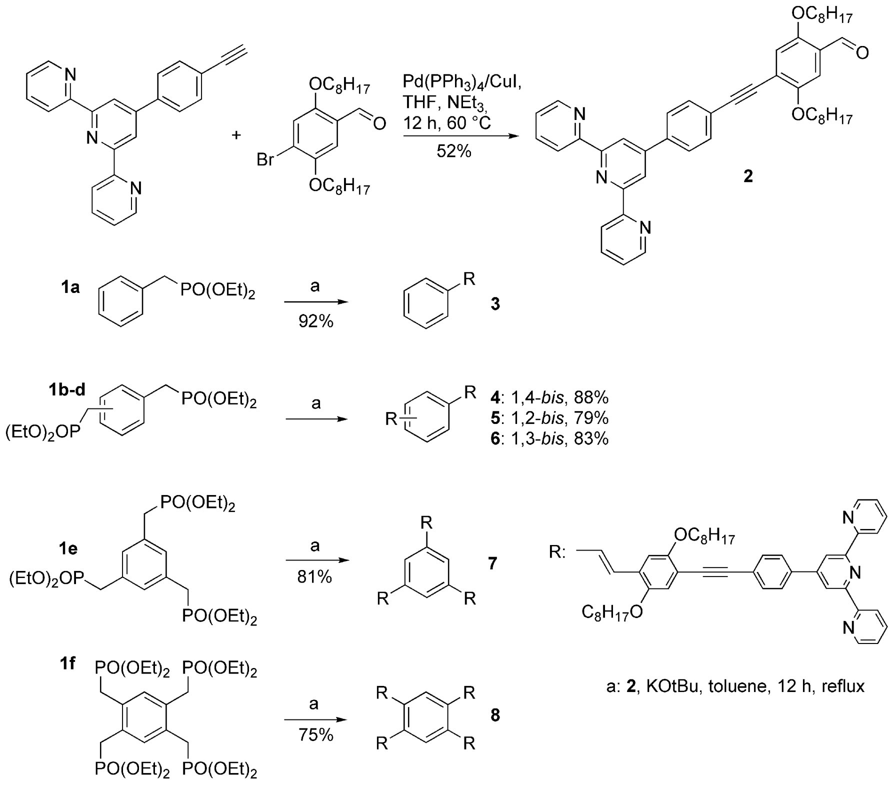


Figure 1. Aromatic region of the ^{1}H NMR spectra of **3** (top) and **4** (bottom). Both spectra: 400 MHz, CDCl$_3$, room temperature.



Scheme 3. Synthesis of the series of π-conjugated terpyridines **3**–**8** by HWE reactions.

be expected, because of the 1,4-substitution and the linear alignment of the overall molecule, the bis(terpyridine) **4** exhibits the most pronounced red shift ($\lambda_{\text{abs,max}}$ = 425 nm), indicating the highest effective conjugation length within the series investigated. It is known from detailed studies on various types of poly(phenylenevinylene)s that the geometries (i.e., the substitution patterns) have an important impact on the overall photophysical properties of the materials.[13] Although the π-conjugated system is also extended for the *ortho*-angular bis(terpyridine) **5**, this is to a minor degree in relation to **4**, due to the kinked arrangement of the two chromophores.[14] In the present case, the influence of the π-extension is overcompensated by the strong steric hindrance and tilt of the two *ortho*-arranged substituents, and so a distinct disturbance of the electron delocalization can be observed, even leading to a blue shift of 2 nm in relation to **3**. Because π-conjugation through *meta* substitution is generally discontinued,[15] the bis(terpyridine) **6** and the tris(terpyridine) **7** show only relatively small red shifts in their absorption maxima. From an electronic point of view, these compounds feature π-conjugated systems similarly as effective as that of the mono(terpyridine) **3**.

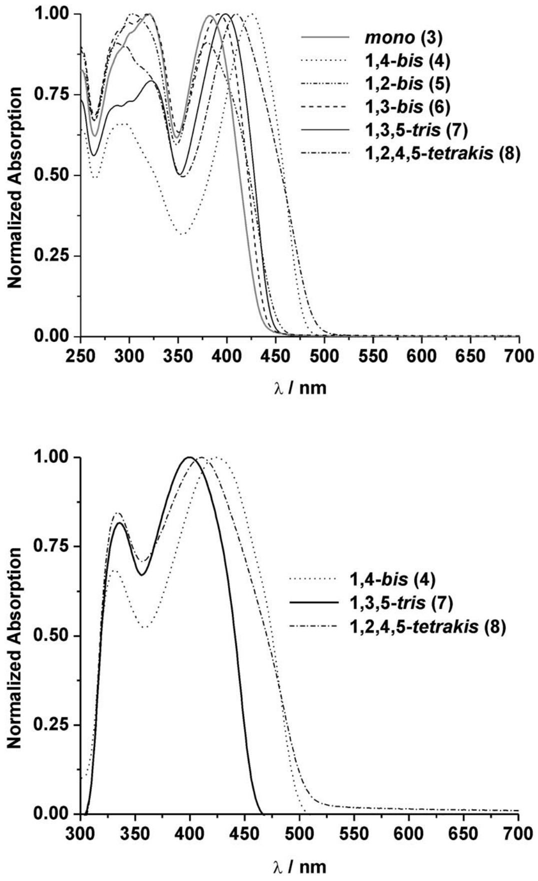


Figure 2. Top: Normalized absorption spectra of oligo(terpyridine)s **3**–**8** in dilute solution (all spectra 10^{-6} M in $CHCl_3$). Bottom: Normalized absorption spectra of oligo(terpyridine)s **4**, **7**, and **8** in the solid state (thin solid films on glass substrates). All spectra were measured at room temperature.

Table 3. Absorption properties of the oligo(terpyridine)s **3**–**8** in dilute solution and in the solid state.

Entry	λ_{abs} [nm] Solution[a]	Film[b]	$\varepsilon \times 10^7$ [$\text{cm}^2\,\text{mol}^{-1}$][a]	E_g^{opt} [eV][c] Solution[a]	Film[b]
3	380	–[d]	3.3	2.86	–[d]
4	425	427	10.0	2.61	2.51
5	378	–[d]	6.9	2.77	–[d]
6	392	–[d]	6.1	2.84	–[d]
7	398	399	13.2	2.80	2.71
8	409	410	11.3	2.57	2.47

[a] 10^{-6} M in $CHCl_3$ at room temperature. [b] Thin solid films on glass substrates at room temperature. [c] Estimated from the absorption spectra by extrapolation of the tails of the lower energy levels. [d] The films were not investigated because of inhomogeneity.

In general, the rise in the extinction coefficients is partially attributable to the increasing numbers of chromophores per molecule. However, the growth in intensity (S[16]) of the absorption bands appears to be more than proportionate (Table 4). The largest step is found between **3** and **4**, once more emphasizing the electronic communication through the entire molecule. The intensities per terpyridine side-chain for **3** and for the *meta* derivative **6** are in the same range; for the tris(terpyridine) **7** a slightly increased intensity is observed. The values for the bandwidth (b) are in the 4650 ± 350 cm^{-1} range, except for **5** and **8** (5089 cm^{-1} and 6006 cm^{-1}, respectively). This broadening of the absorption maximum can be unambiguously explained by strong *intra*molecular steric interaction between the neighboring terpyridine side-chains.

The tetrakis(terpyridine) **8** combines both *ortho* and *para* substitution within one molecular structure, so the electronic and steric effects discussed above independently for **4** and **5** now have to be considered simultaneously. Generally, such cross-shaped chromophores cannot simply be described as superpositions of two linear analogues.[17] Although the global picture appears to be more complex and is currently under investigation,[18] a few basic characteris-

Table 4. Characteristics of the longest-wavelength absorption maxima of the oligo(terpyridine)s **3**–**8** in dilute solution.[a]

Entry	λ_{abs} [nm]	$\varepsilon \times 10^7$ [$\text{cm}^2\,\text{mol}^{-1}$]	Half-width b [cm^{-1}][b]	Intensity S[c] [10^{11} cm mol^{-1}]	S per terpyridine unit [10^{11} cm mol^{-1}]
3	380	3.3	4296	1.41	1.41
4	425	10.0	4390	4.37	2.18
5	378	6.9	5348	3.67	1.83
6	392	6.1	5089	3.08	1.54
7	398	13.2	4889	6.45	2.15
8	409	11.3	6006	6.79	1.70

[a] 10^{-6} M in $CHCl_3$ at room temperature. [b] Estimated by linear extrapolation of the low-wavelength value. [c] Calculated: $S = b\varepsilon$.

tics can be addressed. The *para* arrangement of the π-conjugated systems is expressed by a pronounced red shift of $\lambda_{abs,max}$ of about 30 nm relative to **3**. Concurrently, the *ortho* substitution pattern, resulting in torsions of the substituents relative to each other, mainly leads to a considerable decrease in the intensity with respect to the number of terpyridine side-chains. The optical bandgaps (E_g^{opt}) were estimated from the absorption spectra by extrapolation of the tails on the longer-wavelength side (i.e., at 10% absorption). The E_g^{opt} values for bis(terpyridine) **4** and tetrakis(terpyridine) **8** are significantly lower than those for the other derivatives (2.61 eV and 2.57 eV, respectively). This additionally shows that – thanks to the *para* linkages of the terpyridine groups – the effective π-conjugated system is extended. The bandgaps determined for the *meta*-substituted compounds **6** and **7** are comparable to the value for the simple mono(terpyridine) **3** (2.86 eV).

No significant changes in the absorption behavior of the π-conjugated systems were detected for the thin solid films of the three oligo(terpyridine)s investigated (Figure 2, bottom). From this we conclude that the structural and electronic characteristics discussed for the corresponding dilute solutions can also be observed in the solid state.

The photoluminescence (PL) spectra and the absolute quantum yields (Φ_{PL}[19]) of the series of terpyridines were also studied, and the results are summarized in Table 5. All PL spectra and the Φ_{PL} values were obtained upon excitation at the corresponding absorption maximum. The PL spectra of the oligo(terpyridine)s are also strongly influenced by the numbers of attached π-conjugated terpyridine moieties and the substitution patterns of the central phenyl rings. Because of the *meta* substitution in **6** and **7**, the conjugated side groups have to be treated as isolated chromophores rather than as uniform chromophores, with their structures resembling that of the mono(terpyridine) **3**. The maxima of the emission bands ($\lambda_{PL,max}$) of these three derivatives (**3**, **6**, and **7**) are therefore located at about 445 nm, displaying a bright blue color (Figures 3 and 4). As in the case of the extinction coefficient ε, the increase in Φ_{PL} for **6** and **7** relative to **3** is attributable to the increasing numbers of chromophores within the molecules (Tables 4 and 5). A remarkably high quantum yield of 0.98 and a red shift of the emission maximum of about 40 nm relative to **3** was determined for the linear bis(terpyridine) **4**. As a consequence of its long effective conjugation length, **4** emits with an intense cyan color ($\lambda_{PL,max}$ = 482 nm, Stokes shift: 2780 cm^{-1}, see Figures 3 and 4).[10a,10b]

Table 5. PL properties of the oligo(terpyridine)s **3**–**8** in dilute solution and in the solid state.

Entry	$\lambda_{sol,film}$ [nm][a]	Δ^S_{sol} [cm^{-1}]	$\Phi_{PL,sol}$ [a,c]	$\lambda_{PL,film}$ [nm][b,c]	Δ^S_{film} [cm^{-1}]	$\Phi_{PL,film}$ [b,c,d]
3	445	3840	0.80	–[e]	–[e]	–[e]
4	482	2780	0.98	538	4830	0.48
5	462	4810	0.84	–[e]	–[e]	–[e]
6	445	3040	0.85	–[e]	–[e]	–[e]
7	445	2650	0.87	507	5340	0.15
8	496	4290	0.53	555	6370	0.18

[a] Ca. 10^{-6} M in $CHCl_3$ at room temperature. [b] Thin solid films on glass substrates at room temperature. [c] Absolute quantum yields; uncorrected with respect to reabsorption. [d] Absolute quantum yields in the solid state (see ref. 19); uncorrected with respect to reabsorption. [e] The films were not investigated because of their inhomogeneity.

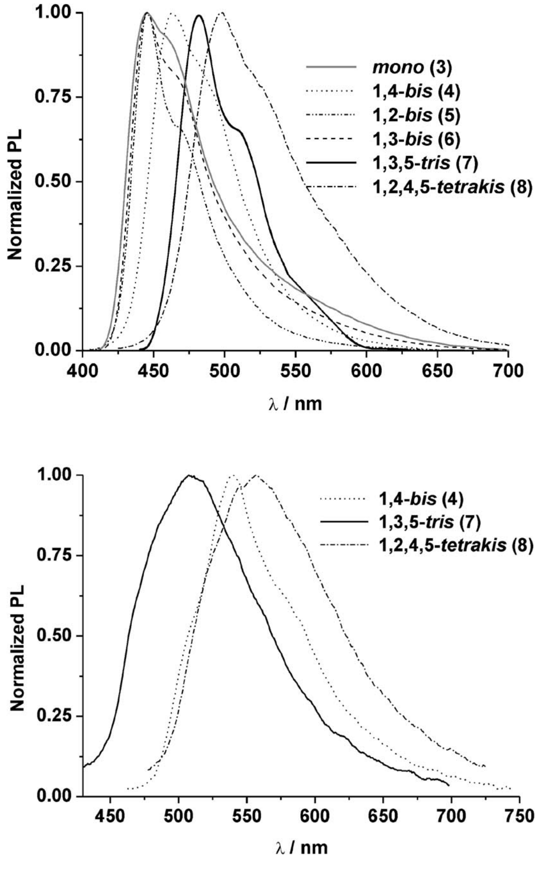


Figure 3. Top: normalized photoluminescence spectra of oligo(terpyridine)s **3**–**8** in dilute solution (10^{-6} M in $CHCl_3$ for all spectra). Bottom: normalized photoluminescence spectra of the oligo(terpyridine)s **4**, **7**, and **8** in the solid state (thin solid films on glass substrates).

For the *ortho*-substituted bis(terpyridine) **5**, a large Stokes shift of 4810 cm^{-1} can be observed ($\lambda_{PL,max}$ = 462 nm). As can be seen from the absorption behavior, a distinct tilt of the conjugated side groups, due to strong steric hindrance, would be expected for the ground state (S_0). We assume that the molecular geometry is changed in the excited state (S_1) and that the overall π-conjugated system could consequently be enlarged significantly.[19] The same effect was observed for the tetrakis(terpyridine) **8**. To the best of our knowledge, green emitting oligo(terpyridine)s have not previously been reported in the literature. Because of its large Stokes shift of almost 4290 cm^{-1} the star-shaped terpyridine **8** features a bright green emission ($\lambda_{abs,max}$ = 409 nm, $\lambda_{PL,max}$ = 496 nm) with high quantum yields (Φ_{PL} = 0.53).

The results from NMR spectroscopy indicate that aggregation of the molecules is strongly discouraged in dilute solutions thanks to the solubilizing alkoxy groups. However, aggregation cannot be fully prevented in the solid

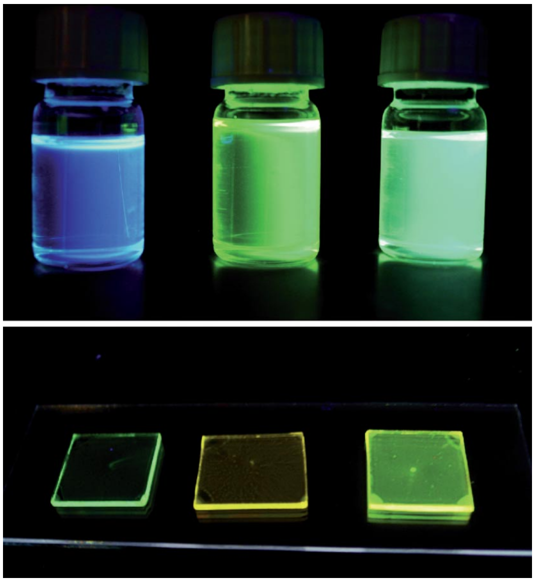


Figure 4. Representation of the photoluminescence (excitation at 375 nm) of dilute solutions (top) and thin solid films (bottom). For both representations: **7** (left), **8** (middle), and **4** (right).

state. Here, pronounced red shifts (50–60 nm) of the emission maxima relative to the dilute solutions were observed for **4**, **7**, and **8** (Table 4, Figure 3). All thin spin-coated films show emissions with their maxima in the 507 to 555 nm range. While bis(terpyridine) **4** still features a strong cyan emission ($\Phi_{\mathrm{PL}} = 0.48$), for the star-shaped derivatives **7** and **8** the emission in the solid state is reduced significantly.

Conclusions

A series of mono-, bis-, tris-, and tetrakis(terpyridine)s based on a common rigid π-conjugated building block has been synthesized by straightforward Horner–Wadsworth–Emmons reactions. The numbers of conjugated terpyridine-based side groups and the overall geometries of the molecules have a distinct influence on their photophysical properties in dilute solution and in the solid state. The highest effective conjugation length within the series was observed for the rigid-linear bis(terpyridine). For the *ortho*-substituted linear and star-shaped derivatives, significant changes in the molecular structure upon excitation have been deduced from the photophysical investigations. All compounds exhibited strong blue to green emission with very high quantum yields in solution. In the solid state, three different emission colors – cyan, green, and orange – were observed. Overall, the π-conjugated oligo(terpyridine)s shown here are promising candidates for the design of functional materials and, in combination with transition metal complexation, suitable building blocks for the construction of functional supramolecular assemblies and metallo-polymers with potential for, for example, optoelectronic applications.

Experimental Section

General: Unless stated otherwise, all reagents were purchased from commercial sources and were used without further purification. The solvents were obtained from Biosolve and were dried and distilled by standard procedures. Chromatographic separations were performed on aluminium oxide (neutral, Macherey–Nagel, 0.063–0.200 mm). The set of benzylic phosphonates **1**[10] and the aldehyde-functionalized terpyridine **2**[9a] were prepared by known procedures (see Supporting Information for details).

Instrumentation: ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in deuterated solvents (Cambridge Isotope Laboratories, Inc.) at 25 °C on a Varian Mercury 400 MHz instrument. Chemical shifts are reported in ppm downfield from TMS (^{1}H and ^{13}C NMR) and H_3PO_4 (^{31}P NMR). Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-ToF MS) was performed on a Voyager-DE PRO biospectrometry workstation (Applied Biosystems) time-of-flight mass spectrometer, with dithranol as matrix. Elemental analysis was obtained with a EuroVector EuroEA3000 elemental analyzer for CHNS-O. UV/Vis spectra were measured with a Perkin–Elmer Lambda-19 spectrometer, photoluminescence spectra were recorded with a Perkin–Elmer LS50B luminescence spectrometer. Absolute quantum yields were obtained with a Hamamatsu Photonic Multi-Channel Analyzer C10027. For these techniques concentrations of 10^{-6} M in degassed $CHCl_3$ (1 cm cuvette) at 25 °C were used. Thin solid films were spin-coated on glass substrates from $CHCl_3$ solutions with concentrations of ca. 2.5 mg mL^{-1}. A Laurell Technologies WS 400/500 Series spin-coater was used; the spin-coating rate was 1000 rpm for 30 s. The glass slides were cleaned by consecutive ultrasonication in water, acetone, and isopropanol (each 15 min) prior to use. Film thicknesses were determined with an optical profilometer (Fogale Zoomsurf).

General Procedure for the HWE Reaction: The synthesis of terpyridines **3**–**8** was performed as follows: KO^{t}Bu (1.05 equiv. per phosphonate group of **1**) was added to a solution of a benzylic phosphonate **1** (0.5 mmol) and **2** (1 equiv. per phosphonate group of **1**) in dry and degassed toluene (50 mL). The reaction mixture was heated at reflux for 12 h, allowed to cool to room temperature, and extracted with brine (3 × 15 mL). The organic phase was dried with anhydrous $MgSO_4$ and then concentrated. The residue was triturated with methanol to yield the crude products, which were further purified by column chromatography (neutral alumina, CH_2Cl_2/MeOH as eluent).[9a]

4′-(4-{[2,5-Bis(octyloxy)-4-styrylphenyl]ethynyl}phenyl)-2,2′:6′,2′′-terpyridine (3): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 2 H, 3′-/5′-H), 8.75 (d, ^{3}J = 4.2 Hz, 2 H, 6-/6′′-H), 8.69 (d, ^{3}J = 8.0 Hz, 2 H, 3-/3′′-H), 7.91 (m$_c$, 4 H, 4-/4′′-H, H$_{aryl}$), 7.68 (d, ^{3}J = 8.1 Hz, 2 H, H$_{aryl}$), 7.54 (d, ^{3}J = 7.5 Hz, 2 H, H$_{aryl}$), 7.47 (d, ^{3}J = 15.8 Hz, 1 H, H$_{olefin}$), 7.37 (m$_c$, 4 H, 5-/5′′-H, H$_{aryl}$), 7.26 (m$_c$, 1 H, H$_{aryl}$), 7.17 (d, ^{3}J = 15.8 Hz, 1 H, H$_{olefin}$), 7.15 (s, 1 H, H$_{aryl}$), 7.05 (s, 1 H, H$_{aryl}$), 4.12 (t, ^{3}J = 6.8 Hz, 2 H, H$_{alkyl}$), 4.03 (t, ^{3}J = 6.8 Hz, 2 H, H$_{alkyl}$), 1.88 (m$_c$, 4 H, H$_{alkyl}$), 1.61 (m$_c$, 4 H, H$_{alkyl}$), 1.44–1.27 (m, 16 H, H$_{alkyl}$), 0.88 (m$_c$, 6 H, H$_{alkyl}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1, 155.5, 152.8, 151.9, 149.0, 145.6, 142.3, 137.8, 137.3, 133.1, 128.9, 128.6, 128.4, 127.8, 124.8, 124.0, 123.7, 123.5, 120.9, 118.1, 117.8, 115.3, 112.0, 111.2, 97.5, 83.9, 68.8, 32.1, 29.7, 29.6, 29.3, 25.7, 22.8, 14.3 ppm. MALDI-ToF MS (dithranol): *m*/*z* = 768.59 [M + H]$^+$. $C_{53}H_{57}N_3O_2$ (768.0): calcd. C 82.88, H 7.48, N 5.47; found C 83.01, H 7.35, N 5.32.

1,4-Bis(4-{[4-(2,2′:6′,2′′-terpyridin-4′-yl)phenyl]ethynyl}-2,5-bis(octyloxy)styryl)benzene (4): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 4 H, 3′-/5′-H), 8.75 (d, ^{3}J = 5.4 Hz, 4 H, 6-/6′′-H), 8.69 (d, ^{3}J

= 8.2 Hz, 4 H, 3-/3′′-H), 7.91 (m_c, 8 H, 4-/4′′-H, H_{aryl}), 7.68 (d, ^3J = 8.7 Hz, 4 H, H_{aryl}), 7.54 (s, 4 H, H_{aryl}), 7.50 (d, ^3J = 16.6 Hz, 2 H, H_{olefin}), 7.37 (m_c, 4 H, 5-/5′′-H), 7.18 (d, ^3J = 16.9 Hz, 2 H, H_{olefin}), 7.16 (s, 2 H, H_{aryl}), 7.06 (s, 2 H, H_{aryl}), 4.13 (t, ^3J = 5.8 Hz, 4 H, H_{alkyl}), 4.04 (t, ^3J = 6.7 Hz, 4 H, H_{alkyl}), 1.90 (m_c, 8 H, H_{alkyl}), 1.68–1.52 (m, 8 H, H_{alkyl}), 1.46–1.25 (m, 32 H, H_{alkyl}), 0.92–0.85 (m, 12 H, H_{alkyl}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 155.2, 153.0, 152.1, 148.7, 145.5, 142.4, 137.2, 136.5, 133.3, 129.1, 128.5, 124.7, 124.2, 123.8, 123.4, 121.1, 117.9, 117.8, 115.2, 112.1, 111.1, 98.0, 84.2, 68.7, 32.0, 29.8, 29.7, 29.2, 25.7, 22.8, 14.3 ppm. MALDI-ToF MS (dithranol): m/z = 1457.97 $[M + H]^+$. $C_{100}H_{108}N_6O_4$ (1458.0): calcd. C 82.38, H 7.47, N 5.76; found C 82.52, H 7.64, N 5.52.

1,2-Bis(4-{[4-(2,2′:6′,2′′-terpyridin-4′-yl)phenyl]ethynyl}-2,5-bis-(octyloxy)styryl)benzene (5): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 4 H, 3′-/5′-H), 8.75 (d, ^3J = 5.9 Hz, 4 H, 6-/6′′-H), 8.68 (d, ^3J = 8.0 Hz, 4 H, 3-/3′′-H), 7.92 (m_c, 8 H, 4-/4′′-H, H_{aryl}), 7.69 (d, ^3J = 8.5 Hz, 4 H, H_{aryl}), 7.68 (m_c, 4 H, H_{aryl}), 7.48 (d, ^3J = 16.1 Hz, 2 H, H_{olefin}), 7.36 (m_c, 4 H, 5-/5′′-H), 7.17 (d, ^3J = 16.2 Hz, 2 H, H_{olefin}), 7.14 (s, 2 H, H_{aryl}), 7.07 (s, 2 H, H_{aryl}), 4.14 (t, ^3J = 6.5 Hz, 4 H, H_{alkyl}), 4.08 (t, ^3J = 6.4 Hz, 4 H, H_{alkyl}), 1.88 (m_c, 8 H, H_{alkyl}), 1.69–1.54 (m, 8 H, H_{alkyl}), 1.44–1.21 (m, 32 H, H_{alkyl}), 0.95–0.82 (m, 12 H, H_{alkyl}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 155.6, 153.1, 152.0, 149.2, 145.7, 142.5, 137.2, 134.8, 133.4, 128.4, 128.2, 127.9, 124.7, 124.1, 123.5, 123.3, 121.2, 118.5, 117.9, 115.4, 111.8, 111.5, 97.2, 84.5, 69.2, 32.3, 30.0, 29.7, 29.3, 25.7, 22.9, 14.1 ppm. MALDI-ToF MS (dithranol): m/z = 1457.95 $[M + H]^+$. $C_{100}H_{108}N_6O_4$ (1458.0): calcd. C 82.38, H 7.47, N 5.76; found C 82.19, H 7.22, N 5.87.

1,3-Bis(4-{[4-(2,2′:6′,2′′-terpyridin-4′-yl)phenyl]ethynyl}-2,5-bis-(octyloxy)styryl)benzene (6): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 4 H, 3′-/5′-H), 8.74 (d, ^3J = 5.7 Hz, 4 H, 6-/6′′-H), 8.67 (d, ^3J = 8.2 Hz, 4 H, 3-/3′′-H), 7.91 (m_c, 8 H, 4-/4′′-H, H_{aryl}), 7.68 (d, ^3J = 8.5 Hz, 4 H, H_{aryl}), 7.68 (m_c, 2 H, H_{aryl}), 7.52 (s, 1 H, H_{aryl}), 7.48 (d, ^3J = 15.8 Hz, 2 H, H_{olefin}), 7.36 (m_c, 5 H, 5-/5′′-H, H_{aryl}), 7.16 (d, ^3J = 15.7 Hz, 2 H, H_{olefin}), 7.13 (s, 2 H, H_{aryl}), 7.08 (s, 2 H, H_{aryl}), 4.13 (t, ^3J = 6.8 Hz, 4 H, H_{alkyl}), 4.05 (t, ^3J = 6.7 Hz, 4 H, H_{alkyl}), 1.87 (m_c, 8 H, H_{alkyl}), 1.67–1.55 (m, 8 H, H_{alkyl}), 1.42–1.23 (m, 32 H, H_{alkyl}), 0.96–0.80 (m, 12 H, H_{alkyl}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 155.4, 153.1, 151.5, 148.7, 145.7, 142.5, 138.2, 137.1, 132.8, 128.7, 128.5, 127.7, 124.4, 124.2, 123.8, 123.1, 122.8, 121.0, 117.8, 117.9, 115.4, 111.9, 110.9, 98.0, 84.0, 68.5, 31.8, 29.6, 29.5, 29.3, 25.7, 22.7, 14.2 ppm. MALDI-ToF MS (dithranol): m/z = 1457.96 $[M + H]^+$. $C_{100}H_{108}N_6O_4$ (1458.0): calcd. C 82.38, H 7.47, N 5.76; found C 82.27, H 7.34, N 5.97.

1,3,5-Tris(4-{[4-(2,2′:6′,2′′-terpyridin-4′-yl)phenyl]ethynyl}-2,5-bis-(octyloxy)styryl)benzene (7): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 6 H, 3′-/5′-H), 8.75 (d, ^3J = 5.2 Hz, 6 H, 6-/6′′-H), 8.68 (d, ^3J = 8.0 Hz, 6 H, 3-/3′′-H), 7.90 (m_c, 12 H, 4-/4′′-H, H_{aryl}), 7.67 (d, ^3J = 8.5 Hz, 6 H, H_{aryl}), 7.48 (d, ^3J = 15.9 Hz, 3 H, H_{olefin}), 7.35 (m_c, 6 H, 5-/5′′-H), 7.17 (d, ^3J = 15.9 Hz, 3 H, H_{olefin}), 7.14 (s, 3 H, H_{aryl}), 7.11 (s, 3 H, H_{aryl}), 7.04 (s, 3 H, H_{aryl}), 4.15 (t, ^3J = 6.0 Hz, 6 H, H_{alkyl}), 4.01 (t, ^3J = 6.7 Hz, 6 H, H_{alkyl}), 1.92–1.82 (m, 12 H, H_{alkyl}), 1.70–1.51 (m, 12 H, H_{alkyl}), 1.48–1.20 (m, 48 H, H_{alkyl}), 0.95–0.82 (m, 18 H, H_{alkyl}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 155.2, 153.1, 151.5, 148.9, 145.7, 142.1, 137.0, 136.1, 133.3, 128.1, 124.9, 124.3, 123.9, 123.5, 122.5, 121.2, 118.5, 117.9, 115.1, 111.9, 111.1, 97.1, 84.2, 68.9, 32.0, 30.0, 29.9, 29.1, 25.6, 22.5, 14.1 ppm. MALDI-ToF MS (dithranol): m/z = 2147.29 $[M + H]^+$. $C_{147}H_{159}N_9O_6$ (2147.9): calcd. C 82.20, H 7.46, N 5.87; found C 82.05, H 7.61, N 6.02.

1,2,4,5-Tetrakis(4-{[4-(2,2′:6′,2′′-terpyridin-4′-yl)phenyl]ethynyl}-2,5-bis(octyloxy)styryl)benzene (8): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 8 H, 3′-/5′-H), 8.74 (m_c, 8 H, 6-/6′′-H), 8.67 (d, ^3J = 8.2 Hz, 8 H, 3-/3′′-H), 7.90 (m_c, 16 H, 4-/4′′-H, H_{aryl}), 7.67 (d, ^3J = 7.9 Hz, 8 H, H_{aryl}), 7.44 (d, ^3J = 16.2 Hz, 4 H, H_{olefin}), 7.34 (m_c, 8 H, 5-/5′′-H), 7.25 (s, 2 H, H_{aryl}), 7.15 (d, ^3J = 15.8 Hz, 4 H, H_{olefin}), 7.12 (s, 4 H, H_{aryl}), 7.04 (s, 4 H, H_{aryl}), 4.10 (m_c, 8 H, H_{alkyl}), 4.05 (m_c, 8 H, H_{alkyl}), 1.95–1.83 1.88 (m, 16 H, H_{alkyl}), 1.66–1.52 (m_c, 16 H, H_{alkyl}), 1.47–1.23 (m, 64 H, H_{alkyl}), 0.95–0.85 (m, 24 H, H_{alkyl}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 155.3, 153.1, 152.1, 149.3, 145.4, 142.1, 137.1, 134.1 133.3, 128.5, 124.5, 124.2, 123.8, 123.3, 122.7, 121.2, 117.9, 117.5, 115.1, 112.2, 111.5, 97.9, 84.2, 69.1, 32.0, 29.8, 29.6, 29.1, 25.5, 22.9, 14.2 ppm. MALDI-ToF MS (dithranol): m/z = 2836.68 $[M + H]^+$. $C_{194}H_{210}N_{12}O_8$ (2837.8): calcd. C 82.11, H 7.46, N 5.92; found C 82.35, H 7.66, N 6.11.

Supporting Information (see footnote on the first page of this article): Synthesis and full characterization of all described compounds, ^{1}H NMR spectra of all compounds and selected additional spectra.

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[19] In previous work we have compared the PL spectra and absolute quantum yields of thin films obtained with a Hamamatsu Photonic Multi-Channel Analyzer C10027 with those measured on a homemade setup. The data obtained in this manner have been found to be consistent within the experimental variance. According to the methods of De Mello (*Adv. Mater.* **1997**, *9*, 230–232) and Pålsson (*Adv. Mater.* **2002**, *14*, 757–758) this system is fitted with an integrating sphere inserted in an Edinburgh Analytical Instruments CD900FS fluorescence spectrometer. A custom-designed integrating sphere (model 05–105, AMKO) with an inner diameter of 105 mm coated inside with $BaSO_4$ was used. For those purposes, excitation was carried out with a tungsten lamp of variable intensity in order to provide suitable conditions to measure the fluorescence of the sample and the scattered excitation light with the same slit widths of the spectrometer. For further information see: E. Tekin, D. A. M. Egbe, J. M. Kranenburg, C. Ulbricht, S. Rathgeber, E. Birckner, N. Rehmann, K. Meerholz, U. S. Schubert, *Chem. Mater.* **2008**, *20*, 2727–2735.

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