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A Facile Route to Bis(pyridyl-1,3,5-triazine) Ligands with Fluorescing Properties

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We present a general method for the preparation of bis(pyridyl-1,3,5-triazine) (dpt) ligands via Stille coupling chemistry. The synthetic procedure surpasses known trimerisation procedures in terms of yield, flexibility, and diversity, as ditopic ligands with different spacers are now available. Polythiophene spacers give rise to different colours by extending the conjugated system and increasing HOMO energy levels. The luminescence properties can be tuned by the spacers, the emission is found in the region from 300–550 nm with nanosecond lifetimes. Preliminary experiments indicate thermochromic properties for the dpt-Fe^{II} complexes.

Introduction

2,2′:6′,2′′-Terpyridine (tpy) and related metallo-supramolecular assemblies have attracted remarkable interest over the last 20 years. In fact, tpy is now one of the most important motifs in metallo-supramolecular chemistry.[1] Although tpy binds many transition metal ions, ruthenium tpy complexes have attracted considerable attention due to their photophysical properties.[2] These properties are altered by exchanging the central pyridine in tpy with 1,3,5-triazine (trz).[3] For example, the ruthenium complex of the ligand 2,4-(dipyridyl-2′-yl)-6-phenyl-1,3,5-triazine (Ph-dpt) possesses a longer metal-to-ligand charge transfer (MLCT) luminescence lifetime than in Ru-tpy complexes. The additional nitrogen atoms in trz are co-planar with the 6-phenyl group, which increases the electronic delocalization. As a result, the energy difference between the emitting ^{3}MLCT state and the deactivating triplet metal-centered state (^{3}MC) is increased, thus lowering Franck–Condon factors and improving emission properties. As a second positive effect, the π-accepting nature of the trz ligand further reduces the energy of the ^{3}MLCT state and the energy gap ΔE between the ^{3}MLCT and ^{3}MC states. Besides the mentioned photophysical properties[4] dpt-based complexes also show thermochromic properties[5] and can be used as hosts for assorted molecules.[6] Ligands with two dpt units are promising candidates for photoactive coordination polymers[7] or metal–organic frameworks.[8] Metallo-polymers based on the analogous ditopic tpy are well-known for their tunable and stimuli-responsive properties.[9]

In contrast to expectation based on their many potential uses, only a few ditopic dpt molecules are known in the literature.[10] The synthesis is based on the trimerisation reaction of the central ring and generally affords low yields of only about 10%. For example, dpt-phenyl-dpt is prepared by reaction of 2-cyanopyridine and 1,4-dicyanobenzene resulting in a product yield of 16%.[10a] These low yields limit full characterization and exploitation of material properties (e.g. rheological measurements); larger amounts of material are clearly needed for the potential of these species to be realized. The low synthetic flexibility hinders the preparation of a wide range of related structures, which are necessary to investigate structure–property relationships. For these reasons we established an improved synthetic route to ditopic dpt ligands. This route should be both highly adaptable and effective. In this report we focus on the incorporation of oligothiophenes into the dpt framework inspired by their remarkable fluorescence properties.[11,12]

Results and Discussion

The known syntheses featuring the 2,4-di(pyridin-2-yl)-1,3,5-triazine (dpt) motif are usually based on trimerisation of nitriles.[13] For example, three equivalents of 2-cyanopyridine react under ring closure conditions to afford 2,4,6-tri(pyridin-2-yl)-1,3,5-triazine.[14] This approach is conve-

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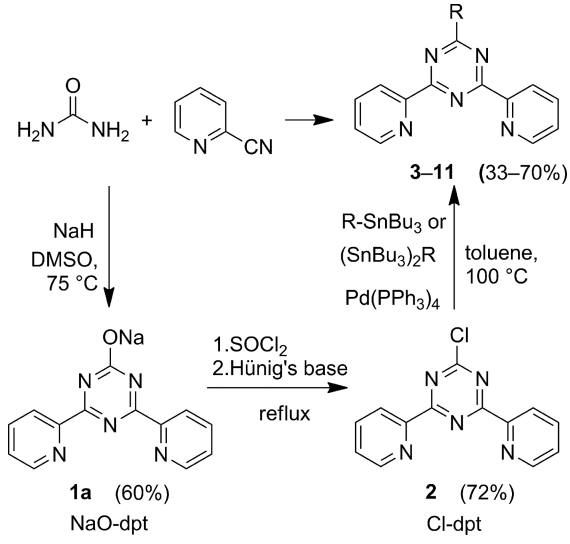
nient for monotopic ligands, but has several drawbacks for ditopic molecules; drawbacks include low yields and difficulty in attaining non-D_3-symmetric molecules. We performed a retrosynthetic analysis of 1′′,4′′-bis[2,4-di(pyridin-2-yl)-1,3,5-triazine-6-yl]benzene (dpt-Ph-dpt) as a reference molecule. To improve the variability of ditopic ligands as well as the reaction yield, we chose to employ a cross-coupling reaction as the last step, which is compatible with the electron poor triazine ring. The coupling takes place between a bis-metal–organic spacer reagent and 6-chloro-dpt, which is available through a nucleophilic substitution of HO-dpt. This approach can be easily applied to different ligands with different spacers as a large number of metal–organic reagents are commercially available. This approach is favored over the synthesis of tin- or boron triazines since these species are considered too unstable.[15] Here, we focus on two main aspects: i) the angle between the two dpt receptors, and ii) the incorporation of conjugated systems. Furthermore, we synthesize precursors and reference molecules based on the dpt motif.

The entire synthetic pathway is shown in Scheme 1. In the first step, 4,6-bis(pyridin-2-yl)-1,3,5-triazine-2-ol (HO-dpt) is obtained as its sodium salt, 4,6-di(pyridin-2-yl)-1,3,5-triazine-2-olate (NaO-dpt) **1a** in 60% yield by the reaction of urea and 2-cyanopyridine.[16] Intermediate **1a** is converted to 2-chloro-4,6-di(pyridin-2-yl)-1,3,5-triazine (Cl-dpt) **2** and subsequent coupling with the stannyl reagents gives desired products **3**–**11** (see Scheme 3). The NaO-dpt salt is characterized by NMR spectroscopy and ESI-MS (positive mode). ^{1}H NMR is in accordance with previously reported spectra.[16]



Scheme 1. Synthetic pathway for dpt-based ligands.

The decomposition temperature of **1a** determined with differential scanning calorimetry is 410 °C, which is exceptionally high. This finding led us to consequently examine the solid-state structure of **1a**. X-ray crystallography confirmed the corresponding sodium salt NaO-dpt. The structure represents a one-dimensional coordination polymer (Supporting Information, Figures S16 and S17). Sodium forms a bond to the dpt pincer as well as to the oxygen atom. Notably, this structure had already been reported by Cao et al.[17] In contrast to the Cao procedure, which involves precipitation with NaCl, our results indicate that the NaO-dpt linkage is formed during the synthesis from urea, 2-cyanopyridine and sodium hydride. Our examination suggests that NaO-dpt forms a type of aggregate in solution. Indeed, NMR experiments revealed a concentration dependence of the proton signals. Figure 1 shows the concentration-dependent ^{1}H NMR spectra of NaO-dpt from 0.18–0.001 M. Higher concentrations resulted in salt precipitation. Signal $H^{3'}$ was found to be shifted upon increasing concentrations to lower field, whereas $H^{6'}$ was shifted to higher field. These concentration-dependent shifts can be explained by inter- and intramolecular interactions.[18] A downfield shift is related to the formation of hydrogen bonds.[19]

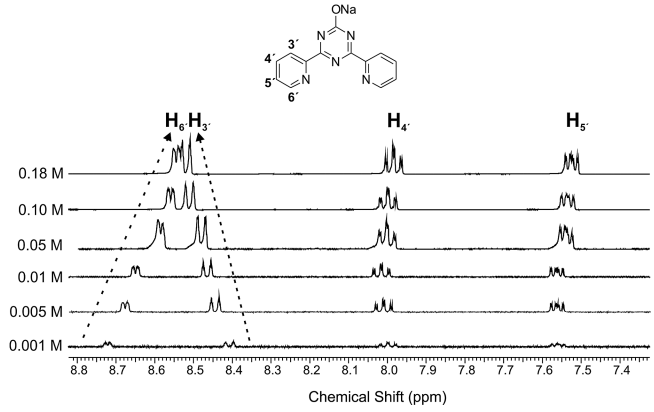
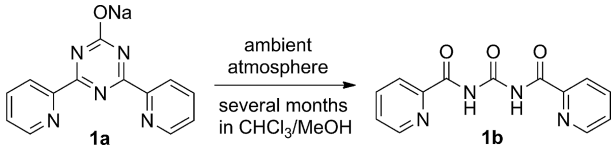


Figure 1. Top: NaO-dpt and assignment of protons. Bottom: Concentration-dependent ^{1}H NMR spectra of NaO-dpt in [D$_6$]DMSO from 0.18 M to 0.001 M at 20 °C.

Most likely, proton $H^{3'}$ forms a bond with one of the nitrogen atoms (N^3 or N^5) in the triazine ring at high concentrations. A shift to a higher field results from evolving π–π interactions and the increased shielding as discussed above (see Figure 1).[20] Although concentration-dependent ^{1}H NMR spectra of triazine derivatives are presented in the literature,[3a] no explanations are given. During crystallization experiments we discovered the hydrolytic instability of the NaO-dpt species. Over several months *N*,*N*′-carbonyldipicolinamide **1b** is formed via hydrolysis in chloroform/methanol, probably catalyzed by trace amounts of chloroform-derived HCl (see Scheme 2). We confirmed the identity of product **1b** by NMR spectroscopy and X-ray crystallography (Supporting Information, Figure S18). Although it is mentioned in the literature, there is currently no reported analytical data for **1b**.[21]

After the preparation of NaO-dpt, we proceeded with the chlorination. Initial chlorination experiments featured thionyl chloride as the chlorinating agent and the pyridine unit in dpt as an intramolecular trapping agent for the HCl resulting from chlorination. Cl-dpt could be deprotonated using the sterically hindered Hünig's base, followed by neutral buffers during work-up. This reaction proceeded in a

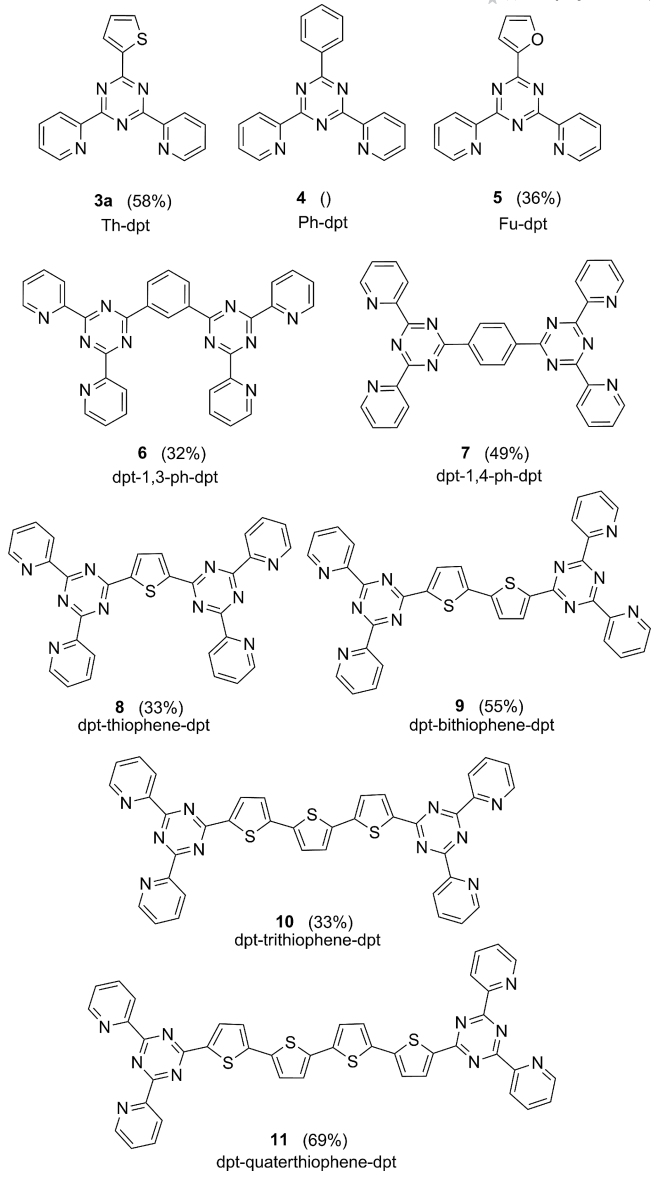


Scheme 2. Degradation of **1a** to *N*,*N*′-carbonyldipicolinamide **1b**.

yield of 72%; the product was fully characterized by ^{1}H- and ^{13}C-NMR spectroscopy as well as by ESI-MS. The ^{1}H NMR spectrum revealed the pyridine pattern of Cl-dpt, whereas ^{13}C displayed a significant shift of C^{6} in the triazine ring due to the chloro group (see Supporting Information/Experimental). ESI-MS further validates the suggested structure with a distinctive chlorine isotope pattern at 270.11 and 272.11 *m*/*z*. Due to the lability of Cl-dpt in basic conditions typically employed for Suzuki-coupling reactions,[22] the Stille coupling was performed under neutral conditions.[23] With this synthetic procedure in hand, we were able to prepare the following dpt-based ligands (see Scheme 3). Whereas the yields of the coupling step are moderate to good, the overall yields range from 13 to 23%. The only known synthesis of **7** using a trimerisation reaction results in a yield of 16% whereas the presented method gives a slightly better overall yield of 20%.

As shown in Scheme 3, our method is versatile in terms of the variability of the central bridge. Furthermore, we were able to incorporate thiophene rings into the dpt system (**3a**, **8**–**11**). Analogous terpyridine systems are known for their photophysical properties.[18] To increase the number of thiophene rings in the bridge, we expanded our methodology to the molecules shown in Scheme 4. For example, 2-thiophenyl-4,6-di(pyridin-2-yl)-1,3,5-triazine (Th-dpt) **3a** is brominated in the 5′′ position with *N*-bromosuccinimide (NBS). Acetic acid was used as solvent to control the regioselectivity.[24] The resulting product **3b** is coupled with the corresponding stannyl reagent. In this way, we prepared dpt-trithiophene-dpt **10** and dpt-quaterthiophene-dpt **11**, having three or four thiophene rings as spacer units, respectively. A useful feature of our synthetic pathway proved to be the simple work-up. Monotopic ligands **3**–**5** are simply extracted from the reaction mixture and washed with toluene, hexane and Et_2O; no further purification is necessary. Workup proved to be even easier with ditopic ligands **6**–**11**. Due to the second dpt pincer ligand, these molecules have an increased tendency to π stack which diminishes solubility[25] and enables facile precipitation from the hot reaction solutions. After washing with toluene, hexane and Et_2O, such ditopic compounds were found to be analytically pure.

All new compounds were fully characterized with different NMR techniques, FT-IR and ESI-MS (for details see Supporting Information). The proton shifts are listed in Table S1. The distinctive pyridine pattern ($H^{3'}$–$H^{6'}$) was observed in all of the molecules. Depending on electron density of the spacer, the corresponding protons are shifted to higher (thiophene and furanyl derivatives) or lower fields (e.g. $H^{3''}$ in **6**). The ^{13}C spectra show similar characteristics.

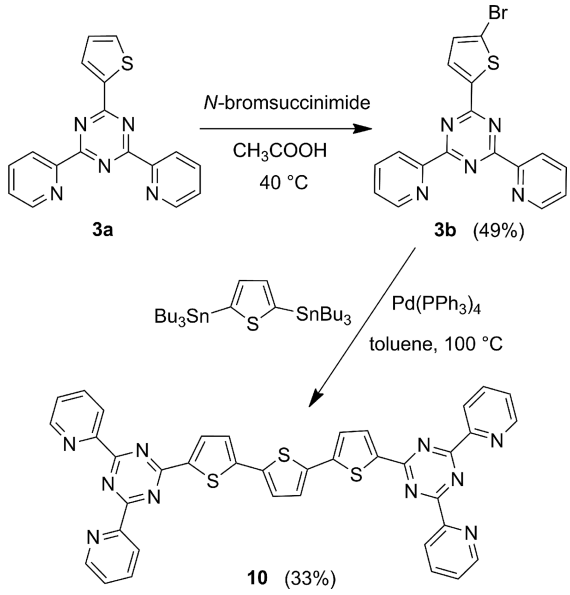


Scheme 3. Overview of new dpt ligands assembled via Stille coupling chemistry.

The triazine related carbon peaks are observed at high frequencies around 170 ppm, whereas the spacer and pyridine units occur between δ = 120 and 150 ppm. ESI-MS confirms the structure of **1**–**11**. Molecules **1**–**11** display the distinctive triazine vibrational modes near 1300 and 1500 cm^{-1}.[26]

In contrast to **4**–**7**, the thiophene containing ligands **8**–**11** have a distinctive color. Monodentate th-dpt (**3a**) is off-white, whereas **8** is greenish white, **9** is yellow and **10** and **11** are dark red. This redshift is apparent in UV/Vis spectra recorded in DCM solution as seen in Figure 2. The thiophene related peak is shifted from 309 nm (**3a**) to 463 nm (**11**) depending on the number of thiophene rings.

For an examination of the HOMO–LUMO gap we performed TD-DFT calculations (for details see Supporting Information Figures S19–S36). Ligands **3a**, **8**, **9**, **10** and **11** are modelled with pyridine groups pointing inward (Sup-



Scheme 4. Synthetic pathway for dpt-trithiophene-dpt **10**.

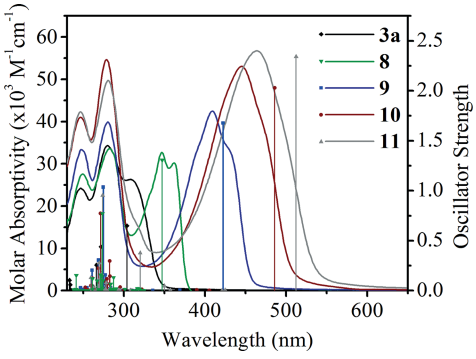


Figure 2. Absorption spectra of **3a** and **8**–**11** in DCM at 25 °C with calculated oscillator strength from TD-DFT as symbols of matching colour.

porting Information, Figure S19). This orientation is not always observed in the solid state and to evaluate the importance of this, the ten possible conformers of ligand **8** are also modelled. The results show that the orientation has little effect on both the calculated transition energies (variation of 2 nm) and the total energy of the molecules, which is smaller than 2 kcal/mol (Supporting Information, Figures S20 and S21). The two absorption bands in the UV region (245 and 280 nm), which are present in all examined samples, are related to the π-π* and n-π* transitions inherent to dpt.[5a] The calculated spectra show absorptions near 230 and 270 nm. The TD-DFT calculations of the thiophene-containing ligands display the same bathochromic shift of the thiophene related band observed in the measured spectra. This transition is attributed to the thiophene conjugated π-system. For **8**–**11** these transitions correspond to the HOMO to LUMO transitions in the molecule. The HOMO has a major contribution of density coming from the thiophene backbone and showed an increase in energy with each thiophene unit added, although it is relatively independent of the triazine (**8** vs. **3a**) (see Figure 3). The LUMO shows the reverse trend; major contribution is made by both triazine groups and increases only slightly with the addition of thiophene units. However, the removal of a triazine moiety pushes the MO to a higher energy leading to its transition into LUMO+1. These two effects contribute to a smaller energy gap with each added thiophene and triazine. The calculated transition follows closely the experimental data, with a greater redshift for the larger molecules due to an exaggeration of the extended delocalization in the modelled system.

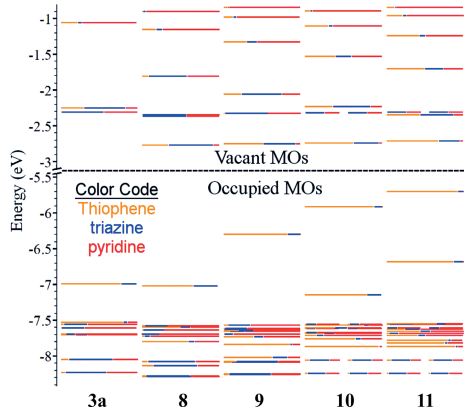


Figure 3. Calculated frontier MO energies of ligands **3** and **8**–**11** obtained from DFT PBE1PBE/6-311G(d,p) with CPCM(CH_2Cl_2).

As seen in Figures 4 and 5, dpt-based polythiophenes show distinctive fluorescence. As expected, the expansion of the π-system results in a redshifted emission. As is evident in Figure 4 tunable emission colours are available.

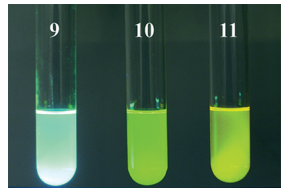


Figure 4. Compounds **9**–**11** in DCM showed under UV light a distinctive fluorescence.

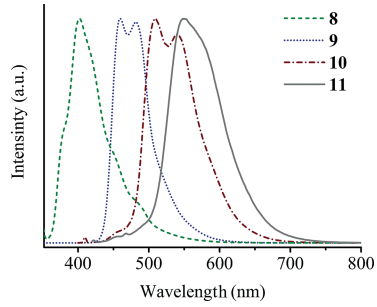


Figure 5. Fluorescence spectra of **8**–**11**. Spectra were recorded at 25 °C in deaerated DCM. The excitation wavelength is 410 nm for **9**–**11** and 350 nm for **8**. All spectra were normalized.

The influence of the dpt unit could be estimated by comparisons with neat oligothiophenes (see Table 1). The dpt unit shifts the absorbance as well as the fluorescence to higher wave numbers.[27] Garcia reported for 2,2′-bithiophene an absorption at 302 nm and an emission at 361 nm.[27a] The corresponding ditopic dpt ligand **9** was found to be shifted to 411 nm (absorption) and 460 nm (emission). The same trend was observed for **10** and **11** and the corresponding polythiophenes. The bathochromic shifts show clearly the influence of the electronegative dpt pincers on the luminescence properties of oligothiophenes. Furthermore, the quantum yield is clearly boosted by the dpt units. Compound **9** possesses a very high quantum yield Φ in relative to bithiophene. The fluorescing molecules possess quantum yields of 60% (**9**), 9% (**10**) and 11.7% (**11**). The lower quantum yields of **10** and **11** are most likely caused by π-π stacking interactions at play in solution. In fact, ESI-MS of **10** revealed the presence of a dimer, whereas **9** does not show any type of aggregation in the gas phase as examined by mass spectrometry. Such π-π interactions in extended π-conjugated systems are associated with an effect called aggregation-caused quenching (ACQ), which is also responsible for weak or non-emissive luminescence properties in solid state.[28]

Table 1. Spectroscopic and photophysical data of **3a** and **8**–**11** in DCM at 25 °C.[a]

	Absorption	Emission			
	λ_{max} thiophene [nm]	λ_{max} [nm]	$\Delta\lambda_{max}$	Φ [%]	$\tau_{1/2}$ [ns]
3a	309	–	–	–	–
8	346	402	56	< 0.1	0.45
9	411	460	49	60	1.30
Bithiophene[27a]	302	361	59	1.8	n.r.
10	445	509	64	9	0.98
Terthiophene[27a]	354	411, 413	79	5.5	0.14
11	463	550	87	11.7	1.42
Quaterthiophene[27a]	390	454, 484	94	16	n.r.

[a] n.r.: not reported.

Indeed **8**–**11** showed no fluorescence in the solid state, in accordance with our hypothesized π–π interactions attributable to the second dpt unit.

Initial complexation experiments with ligands **3a**–**7** and iron(II) acetate resulted in compounds with a distinctive blue colour. In contrast, dpt-dithiophene-dpt **9** and Fe^{II} give, under the same reaction conditions, a dark green compound. Until now it was not possible to determine the molecular structures with NMR, MS or crystallography. Accordingly, it was difficult to identify the molecular reasons for these colour differences. Notably, some of the prepared complexes feature thermochromatic properties. For instance, in going from 10 to 70 °C Fe^{II}-**7** complex (in EtOH) underwent a color change from blue to colorless and UV/Vis measurements (see Supporting Information) revealed a weakening of the MLCT band at 600 nm at temperatures above 40 °C.

Conclusions

In this report we describe a versatile methodology by which to synthesize several new bis-pyridyl-1,3,5-triazine ligands. The newly synthesized Cl-dpt, **2**, is the central building block for further derivatization by organotin reagents via Stille coupling chemistry. We prepared mono- and ditopic ligands with moderate to good yields, with workup generally being straight forward. The introduction of thiophene spacers of different lengths leads to tunable absorption and emission properties. The chelating motive of these ligands, similar to the well-known terpyridines, makes them potential tectons for metallo-supramolecular architectures. Since the bite angle of DPT is larger than that of TPY, it is expected that the ligand field stabilizing energy is lower giving rise to interesting material properties of the resulting metallo-supramolecular assemblies.[29]

Experimental Section

Materials and Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or [D_6]DMSO at 25 °C with a Bruker Fourier 300 spectrometer at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR spectroscopy. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (δ =7.26 ppm for [D]chloroform) and the carbon resonance of the solvent. The assignment of the protons and carbons as well as the corresponding spectra are available in the Supporting Information (Figures S1–S15). Melting points were determined using a Krüss KSP1N. FT-IR Spectra were recorded as KBr pellets in transmission using a Jasco FT/IR-4100. Absorption spectra and emission spectra were measured in deaerated dichloromethane at 25 °C with a Varian Cary 50 UV/Vis-NIR Spectrophotometer and a JASCO FP-8300 Spectrophotometer, respectively. For the luminescence lifetimes, a Photon Technology International TimeMasterTM Model TM-2/2003 fluorescence lifetime spectrometer was used, employing a Hamamatsu PLP2 laser diode as pulse (wavelength output, 415 nm; pulse width, 59 ps). Emission quantum yields were measured at room temperature using the optically dilute method.[30] Coumarin 6 for **9**–**11** and Coumarin 2 for **8** in deaerated dichloromethane solution were used as quantum yield standards, assuming values of 0.78 and 0.68 respectively.[31] Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; emission maxima, ±5 nm; excited state lifetimes, 10%; luminescence quantum yields, 20%. Solvents were removed under reduced pressure using a rotary evaporator unless otherwise stated. All chemicals including the organotin compounds were purchased from Sigma–Aldrich and used as received.

CCDC-1014477 (for **1a**) and -1014478 (for **1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods: All calculations were performed with Gaussian software (G09).[32] The geometry optimization and IR frequency determination was carried out with the DFT method using the PBE1PBE functional[33] and The 6-311G(d,p) basis set[34] associated with the polarized continuum model (CPCM)[35] using DCM as solvent. No imaginary frequencies were observed for all optimized structures confirming the model reached a stable local minimum in energy. The electronic absorption l properties were cal-

culated by TD-DFT approach using the method, basis set and solvent model previously stated. Gaussview 3.09 was used to visualize MOs with an isodensity of 0.02; GaussSum 2.2 was employed to extract the absorption energies, oscillator strengths and molecular orbital energies and Chemissian program was used to sketch energies of MOs with their colour coded atomic orbital (AO) contributions, using 0.001 eV as the threshold for degeneracy for the MO.[36]

Synthesis

Synthesis of 1a: Urea (7.50 g, 0.125 mol) was dissolved in dry DMSO (100 mL) under an inert atmosphere. Sodium hydride (6.00 g, 0.150 mol) (60% dispersion in paraffin oil) was slowly added and the mixture was stirred under an inert atmosphere at 25 °C for 2 h. 2-Cyanopyridine (26.02 g, 0.250 mol) was added to the grey dispersion. The reaction mixture was stirred for 21 h at 75 °C. The resulting black mixture was cooled to 25 °C, poured into ice-water (100 mL) and carefully neutralized with 1 M H_2SO_4. The mixture was cooled for 12 h to increase the yield. The crude product was filtered off and washed with acetone to remove by-products as sodium methylsulfinylmethylide. The filtered solution was saved and stored in the fume hood. After 2–3 days additional product was formed. The two crystallisations fractions were combined and washed with acetone. The resulting product was used without further purification, yield 68% (colourless powder); m.p. > 300 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.59 (ddd, J = 4.8, 1.8, 0.8 Hz, 2 H$^{6'}$), 8.42 (ddd, J = 7.7, 1.3, 1.1 Hz, 2 H$^{3'}$), 7.97 (td, J = 7.7, 1.8 Hz, 2 H$^{4'}$), 7.51 (ddd, J = 7.5, 4.8, 1.3 Hz, 2 H$^{5'}$) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO): δ = 170.51 (C^{2,6}), 169.42 (C^4), 156.15 (C$^{2'}$), 150.05 (C$^{6'}$), 138.23 (C$^{4'}$), 126.35 (C$^{5'}$), 123.59 (C$^{3'}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_3H_{10}N_5O$: 252.08799 [M + H]$^+$ found 252.08816. IR (KBr): $\tilde{\nu}$ = 1540, 1375 (triazine) cm^{-1}.

Synthesis of 1b: Compound **1a** was dissolved in a $CHCl_3$/MeOH (3 mL) and recrystallized by diffusion of Et_2O into the solution. The closed vessel was in the fumehood for about 6 months. The resulting white crystals were filtered off and dried at 25 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 11.85 (s, 2 H, H^1), 8.77 (ddd, J = 4.9, 1.7, 0.9 Hz, 2 H, H$^{6'}$), 8.20 (ddd, J = 7.7, 1.3, 1.1 Hz, 2 H, H$^{3'}$), 8.12 (td, J = 7.7, 1.7 Hz, 2 H, H$^{4'}$), 7.77 (ddd, J = 7.5, 4.9, 1.3 Hz, 2 H, H$^{5'}$) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO): δ = 163.68 (C^2), 148.96 (C$^{6'}$), 147.64 (C$^{2'}$), 147.55 (C^1), 138.57 (C$^{4'}$), 128.40 (C$^{5'}$), 123.19 (C$^{3'}$) ppm.

Synthesis of 2: Freshly distilled thionyl chloride (85 mL, 1.24 mol) was slowly added under an inert atmosphere to 3.50 g (13.9 mmol) **1** NaO-dpt in a Schlenk flask. The reaction mixture was heated to reflux and stirred for 18 h. Thionyl chloride was removed by distillation. Toluene (60 mL) was added and the mixture was distilled to dryness again. The process was repeated twice to remove all thionyl chloride. The resulting off-white triazine salt was suspended in chloroform (60 mL) and diisopropylethylamine (Hünigs base) (4.4 mL, 3.34 g, 25.8 mmol) were added. The orange solution was washed three times with phosphate buffer[37] (150 mL) and brine (60 mL), dried with $MgSO_4$, filtered and evaporated off. The resulting off-white powder product was used without further purification. The product can be recrystallized from hot toluene/hexane (1:2), yield 65% (off-white powder); m.p. 166–172 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.88 (ddd, J = 4.7, 1.8, 0.8 Hz, 2 H, H$^{6'}$), 8.68 (d, J = 7.9 Hz, 2 H, H$^{3'}$), 7.90 (td, J = 7.9, 1.8 Hz, 2 H, H$^{4'}$), 7.50 (ddd, J = 7.6, 4.7, 1.1 Hz, 2 H, H$^{5'}$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 173.65 (C^{2,6}), 172.98 (C^4), 151.63 (C$^{2'}$), 150.83 (C$^{6'}$), 137.36 (C$^{4'}$), 127.27 (C$^{5'}$), 125.55 (C$^{3'}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_{13}H_9N_5Cl$: 270.05410 [M + H]$^+$ found 270.05421. $C_{13}H_8N_5Cl$: C, 57.90; H, 2.99; N, 25.97; found C, 57.45; H, 3.29; N, 25.00. IR (KBr): $\tilde{\nu}$ = 1541, 1370 (triazine) cm^{-1}.

General Synthesis of Monotopic dpt Ligands 3a–5: A solution of Cl-dpt **2** (1.00 g, 3.71 mmol), the corresponding tributylstannyl Bu_3SnR (4.45 mmol) and $Pd(PPh_3)_4$ (0.200 g, 5 mol-%) in degassed toluene (40 mL) were heated for 15 h under an inert atmosphere at 100 °C. The mixture was cooled to room temperature and 1 M NaOH (30 mL) were added. The biphasic mixture was vigorously stirred for 1 h to remove the tin compounds.[38] The phases were separated and the aqueous phase was extracted with chloroform (3 × 30 mL). The combined organic phases were washed with 1 M NaOH (30 mL) and brine (30 mL), dried with $MgSO_4$, filtered and evaporated under reduced pressure. The residue was washed with hot hexane and Et_2O to purify the product.

3a: Yield 58% (off-white powder); m.p. 188–190 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.93 (ddd, J = 4.9, 1.8, 1.1 Hz, 2 H, H$^{6'}$), 8.77 (ddd, J = 7.9, 1.3, 1.3 Hz, 2 H, H$^{3'}$), 8.48 (dd, J = 3.8, 1.3 Hz, 1 H, H$^{3''}$), 7.95 (td, J = 7.8, 1.8 Hz, 2 H, H$^{4'}$), 7.69 (dd, J = 4.9 Hz, 1.3 2 H, H$^{5''}$), 7.54 (ddd, J = 7.6, 4.9, 1.2 Hz, 2 H, H$^{5'}$), 7.26 (t, J = 4.2 Hz, 2 H, H$^{4''}$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 171.30 (C^{2,6}), 168.89 (C^4), 152.95 (C$^{2'}$), 150.19 (C$^{6'}$), 141.01 (C$^{2''}$), 137.13 (C$^{4'}$), 133.07 (C$^{5''}$), 132.57 (C$^{3''}$), 128.67 (C$^{4''}$), 126.45 (C$^{5'}$), 124.84 (C$^{3'}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_{17}H_{11}N_5S$: 318.08017 [M + H]$^+$ found 318.08149. IR (KBr): $\tilde{\nu}$ = 1522, 1373 (triazine) cm^{-1}.

4: Yield 70% (colourless powder); m.p. 227 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.97 (ddd, J = 4.7, 1.8, 0.9 Hz, 2 H, H$^{6'}$), 8.82 (m, 4 H, H$^{3',2''}$), 7.96 (td, J = 7.8, 1.8 Hz, 2 H, H$^{4'}$), 7.58 (m, 5 H$^{5',3'',4''}$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 173.02 (C^{2,6}), 171.74 (C^4), 153.54 (C$^{2'}$), 150.53 (C$^{6'}$), 137.01 (C$^{4'}$), 135.41 (C$^{1''}$), 133.05 (C$^{4''}$), 129.52 (C$^{2''}$), 128.90 (C$^{3''}$), 126.58 (C$^{5'}$), 125.08 (C$^{3'}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_{19}H_{14}N_5$: 312.12437 [M$^+$ + H] found 312.12451. $C_{19}H_{13}N_5$: C, 73.30; H, 4.21; N, 22.24; found C, 72.69; H, 4.16; N, 22.49. IR (KBr): $\tilde{\nu}$ = 1525, 1365 (triazine) cm^{-1}.

5: Yield 36% (off-white powder); m.p. 198–200 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.94 (ddd, J = 4.7, 1.9, 1.0 Hz, 2 H, H$^{6'}$), 8.77 (dd, J = 7.9, 0.9 Hz, 2 H,H$^{3'}$), 7.95 (td, J = 7.8, 1.8 Hz, 2 H, H$^{4'}$), 7.83 (dd, J = 3.5, 0.8 Hz, 1 H, H$^{3''}$), 7.79 (dd, J = 1.8, 0.9 Hz, 1 H, H$^{4''}$), 7.52 (ddd, J = 7.7, 4.7, 1.1 Hz, 2 H, H$^{5'}$), 6.68 (dd, J = 3.5 Hz, 1.8 2 H, H$^{5''}$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 171.56 (C^{2,6}), 165.22 (C^4), 153.13 (C$^{2'}$), 150.51 (C$^{2''}$), 150.48 (C$^{6'}$), 147.27 (C$^{4''}$), 137.06 (C$^{4'}$), 126.39 (C$^{5'}$), 124.90 (C$^{3'}$), 118.19 (C$^{5''}$), 112.83 (C$^{3''}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_{17}H_{11}N_5O$: 302.10364 [M + H]$^+$ found 302.10417. IR (KBr): $\tilde{\nu}$ = 1525, 1365 (triazine) cm^{-1}.

General Synthesis of Ditopic dpt Ligands 6–9: A solution of Cl-dpt **2** (1.00 g, 3.71 mmol), the corresponding bis(tributylstannyl) $(Bu_3Sn)_2R$ (1.85 mmol) and $Pd(PPh_3)_4$ (0.200 g, 5 mol-%) in degassed toluene (40 mL) was heated 15 h under an inert atmosphere at 100 °C. After the reaction the mixture was cooled to room temperature and the precipitate was filtered off and washed with toluene, hot hexane and Et_2O.

6: Yield 32% (grey powder); m.p. > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.19 (m, 1 H, H$^{2''}$), 9.06 (dd, J = 7.7, 0.8 Hz, 2 H, H$^{4''}$), 8.99 (ddd, J = 4.8, 1.8, 1.0 Hz, 4 H, H$^{6'}$), 8.92 (ddd, J = 7.9, 1.3, 1.0 Hz, 4 H, H$^{3'}$), 8.00 (ddd, J = 7.9, 7.7, 1.8 Hz, 4 H, H$^{4'}$), 7.82 (dd, J = 3.5, 0.8 Hz, 1 H, H$^{5''}$), 7.57 (ddd, J = 7.6, 4.8, 1.1 Hz, 4 H, H$^{5'}$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 172.46 (C^4), 171.75 (C^{2,6}), 153.30 (C$^{2'}$), 150.44 (C$^{6'}$), 137.11 (C$^{4'}$), 136.24 (C$^{1'',3''}$), 133.67 (C$^{4''}$), 130.39 (C$^{5''}$), 129.30 (C$^{2''}$), 126.50 (C$^{5'}$),

125.05 ($C^{3'}$) ppm. ESI-MS: *m/z*: calcd. for 545.19452 $[M + H]^+$ found 545.19482. IR (KBr): $\tilde{\nu}$ = 1526, 1356 (triazine) cm^{-1}.

7: Yield 49% (off-white powder); m.p. > 300 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.01 (s 4 H, $H^{2''}$), 8.98 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 4 H, $H^{6'}$), 8.88 (ddd, *J* = 7.9, 1.3, 1.0 Hz, 4 H, $H^{3'}$), 8.01 (ddd, *J* = 7.9, 7.6, 1.8 Hz, 4 H, $H^{4'}$), 7.57 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 4 H, $H^{5'}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 172.45 (C^4), 171.86 ($C^{2,6}$), 153.31 ($C^{2'}$), 150.53 ($C^{6'}$), 139.49 ($C^{1''}$), 137.15 ($C^{4'}$), 129.68 ($C^{2''}$), 126.47 ($C^{5'}$), 125.08 ($C^{3'}$) ppm. ESI-MS: *m/z*: calcd. for 545.19452 $[M + H]^+$ found 545.19485. IR (KBr): $\tilde{\nu}$ = 1525, 1364 (triazine) cm^{-1}.

8: Yield 33% (greenish white powder); m.p. > 300 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.98 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 4 H, $H^{6'}$), 8.84 (ddd, *J* = 7.9, 1.3, 1.0 Hz, 4 H, $H^{3'}$), 8.58 (s, 2 H, $H^{3''}$), 7.99 (ddd, *J* = 7.9, 7.6, 1.8 Hz, 4 H, $H^{4'}$), 7.56 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 4 H, $H^{5'}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 171.70 ($C^{2,6}$), 168.71 (C^4), 152.87 ($C^{2'}$), 150.46 ($C^{6'}$), 146.89 ($C^{2''}$), 137.20 ($C^{4'}$), 133.17 ($C^{3''}$), 126.62 ($C^{5'}$), 125.13 ($C^{3'}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_{30}H_{19}N_{10}S$: 551.15094 $[M^+ + H]$ found 551.15079. IR (KBr): $\tilde{\nu}$ = 1514, 1360 (triazine) cm^{-1}.

9: Yield 55% (yellow powder); m.p. > 300 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.96 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 4 H, $H^{6'}$), 8.79 (ddd, *J* = 7.9, 1.3, 1.0 Hz, 4 H, $H^{3'}$), 8.44 (d, *J* = 4.0 Hz, 2 H, $H^{3''}$), 7.97 (ddd, *J* = 7.9, 7.7, 1.8 Hz, 4 H, $H^{4'}$), 7.54 (m, 6 H, $H^{5'}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 171.56 ($C^{2,6}$), 168.65 (C^4), 153.12 ($C^{2'}$), 150.50 ($C^{6'}$), 143.82 ($C^{2''}$), 140.85 ($C^{5''}$), 137.05 ($C^{4'}$), 133.60 ($C^{3''}$), 126.40 ($C^{5'}$), 126.36 ($C^{4''}$), 125.00 ($C^{3'}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_{34}H_{21}N_{10}S_2$: 633.13866 $[M + H]^+$ found 633.13828. IR (KBr): $\tilde{\nu}$ = 1514, 1373 (triazine) cm^{-1}.

Synthesis of 3b: Compound **3a** (0.500 g, 1.58 mmmol) was dissolved in glacial acetic acid (10 mL). *N*-Bromosuccinimide (0.310 g, 1.73 mmol) was added to the solution and the mixture was stirred at 40 °C for four days under exclusion of light. The resulting greenish suspension was dropwise neutralized with saturated solution of $NaHCO_3$ and extracted with DCM (4 × 25 mL). The combined organic phases were washed with brine, dried with $MgSO_4$ and concentrated to afford **3b**. The product was used without further purification, yield 49% (off-white powder). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.94 (d, *J* = 4.8 Hz, 2 H, $H^{6'}$), 8.73 (d, *J* = 7.8 Hz, 2 H, $H^{3'}$), 8.27 (d, *J* = 4.1 Hz, 1 H, $H^{3''/4''}$), 8.16 (t, *J* = 7.8 Hz, 2 H, $H^{4'}$), 7.74 (dd, *J* = 7.8, 4.8 Hz, 2 H, $H^{5'}$), 7.55 (d, *J* = 4.1 Hz, 1 H, $H^{3''/4''}$) ppm.

Synthesis of 10 and 11: A solution of **3b** (0.267 g, 0.67 mmol), the corresponding bis(tributylstannyl) $(Bu_3Sn)_2R$ (0.34 mmol) and $Pd(PPh_3)_4$ (0.08 g, 10 mol-%) in degassed toluene (20 mL) was heated for 15 h under an inert atmosphere at 100 °C. After the reaction the mixture was cooled to room temperature and the precipitate was filtered off and washed with toluene, hot hexane and Et_2O.

10: Yield 33% (dark red powder); m.p. 239 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.97 (d, *J* = 4.9 Hz, 4 H, $H^{6'}$), 8.78 (d, *J* = 7.7 Hz, 4 H, $H^{3'}$), 8.42 (d, *J* = 4.1 Hz, 2 H, $H^{3''}$), 7.98 (t, *J* = 7.7 Hz, 4 H, $H^{4'}$), 7.56 (dd, *J* = 7.7, 4.9 Hz, 4 H, $H^{5'}$), 7.38 (s, 2 H, $H^{4''}$), 7.38 (d, *J* = 4.1 Hz, 2 H, $H^{3'''}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 171.51 ($C^{2,6}$), 168.65 (C^4), 153.05 ($C^{2'}$), 150.35 ($C^{6'}$), 143.95 ($C^{2''}$), 139.61 ($C^{5''}$), 137.21 ($C^{2'''}$), 137.06 ($C^{4'}$), 133.58 ($C^{4''}$) 126.41 ($C^{5'}$), 126.18 ($C^{3''}$), 125.29 ($C^{3'''}$) 124.93 ($C^{3'}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_{38}H_{23}N_{10}S_3$: 715.12638 $[M + H]^+$ found 715.12666. IR (KBr): $\tilde{\nu}$ = 1573, 1371 (triazine) cm^{-1}.

11: Yield 69% (dark red powder); m.p. 285–289 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.95 (d, *J* = 3.8 Hz, 4 H, $H^{6'}$), 8.79 (d, *J* = 7.6 Hz, 4 H, $H^{3'}$), 8.40 (d, *J* = 3.9 Hz, 2 H, $H^{3''}$), 7.97 (t, *J* = 7.1 Hz, 4 H, $H^{4'}$), 7.53 (t, *J* = 7.6 Hz, 4 H, $H^{5'}$), 7.33 (d, *J* = 3.9 Hz, 4 H, $H^{3''',4'''}$), 7.21 (d, *J* = 3.9 Hz, 2 H, $H^{4''}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 171.46 ($C^{2,6}$), 171.14 (C^4), 153.21 ($C^{2'}$), 150.48 ($C^{6'}$), 139.33 ($C^{2''}$), 137.27 ($C^{2'''}$), 137.02 ($C^{4'}$), 136.16 ($C^{5''}$), 133.66 ($C^{4''}$) 126.33 ($C^{5'}$), 126.12 ($C^{3''}$), 124.95 ($C^{3'''}$,$C^{4'''}$) 124.40 ($C^{3'}$) ppm. HRMS (ESI): *m/z*: calcd. for $C_{42}H_{25}N_{10}S_4$: 797. 11410 $[M + H]^+$ found 797.11385. IR (KBr): $\tilde{\nu}$ = 1509, 1371 (triazine) cm^{-1}.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C spectra, crystallographic data, computational calculation data and UV/Vis spectra.

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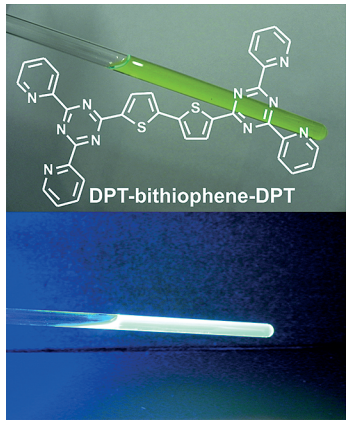
Ligand Synthesis

Several bis(pyridyl-1,3,5-triazine) (dpt) ligands are prepared via Stille coupling with yields and scope of application superior to known trimerisation procedures. Ditopic ligands with different spacers are prepared and incorporation of *p*- and *m*-substituted phenyl rings enable access to different isomers. The absorption and emission properties can be tuned using oligothiophene spacers.



Keywords: Supramolecular chemistry / Synthetic methods / Cross-coupling / N ligands / Luminescence

