DOI: 10.1002/ejoc.200800692

Heteroaromatic Donor–Acceptor π-Conjugated 2,2′-Bipyridines

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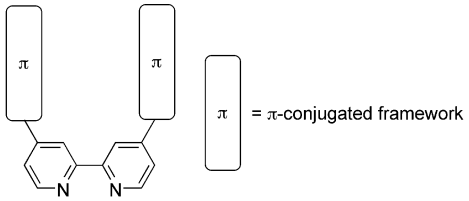
Dedicated to Professor Giorgio A. Pagani for his contribution to heterocyclic chemistry

Keywords: Ligands / Donor-acceptor systems / Heterocycles / Ab initio calculations / Photovoltaics / Dyes

A series of heteroaromatic 4,4′-π-conjugated 2,2′-bipyridines (bpy) bearing conjugated π-excessive and π-deficient heteroaromatic rings as donor (D) and acceptor (A) substituents, respectively, is presented. We have experimentally and computationally found that, upon variation of donor and acceptor properties of the heterocyclic subunits in combination with different structural symmetries (bpy-π-D or bpy-π-D-π-A), the absorption and emission maxima and molecular orbital energy levels can be easily tuned over a broad range. Properties of the new ligands can be efficiently exploited in metal complexes for dye-sensitized solar cells and in other materials for optical applications.

Introduction

Bipyridine is likely the most widely used ligand in chemistry. Among the different isomers, the symmetrical 2,2′-bipyridine (bpy) ligand is the most common ligand and has been extensively used to chelate metal cations to form charged complexes.[1] One of its major features is its ease of functionalization at the pyridine sites for custom-tailored applications. In the last decade metal-bpy complexes have been investigated for application in materials science, including nonlinear optics (NLO)[2] and photovoltaics.[3] For such applications, polar and polarizable bipyridine ligands **1** with extended π-conjugated frameworks are required.[2] Accordingly, Le Bozec and others have investigated 4,4′-π-conjugated bpy ligands **1** and corresponding complexes for II-order NLO applications.[4–6] More recently, Graetzel et al. have used extended π-conjugated bpys as sensitizer components in dye-sensitized solar cells with improved molar extinction coefficients and longevity[7] and as luminescent material.[8]



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Despite this great potential, the vast majority of conjugated ligands are limited to π-donor-substituted 2,2′-bipyridines. This is a strong limitation if one considers that molecular energy levels and structural and electronic properties, which in turn dictate materials' properties (NLO response and solar energy conversion efficiency), closely depend on molecular symmetry and on the presence of polar π-donor (D) and π-acceptor (A) molecular subunits. Besides, with few exceptions,[9] reported D and A components are built around conjugated benzenoid cores and rely on the D and A capacities of simple primary organic functionalities such as OR, NR_2, and NO_2. Indeed, π-deficient and π-excessive heteroaromatics, even the unsubstituted rings, may act as efficient A and D moieties, respectively.[10,11] Their electronic structure may be efficiently tuned by varying the type, number, and position of ring heteroatoms in order to finely tune electronic and optical properties of the ultimate materials.[12] We have already exploited the beneficial effects of heteroaromatic rings in polar chromophores for II- and III-order NLO.[12,13] Recently, dipyrrolyl-functionalized bipyridines have been investigated as anion receptors.[9a]

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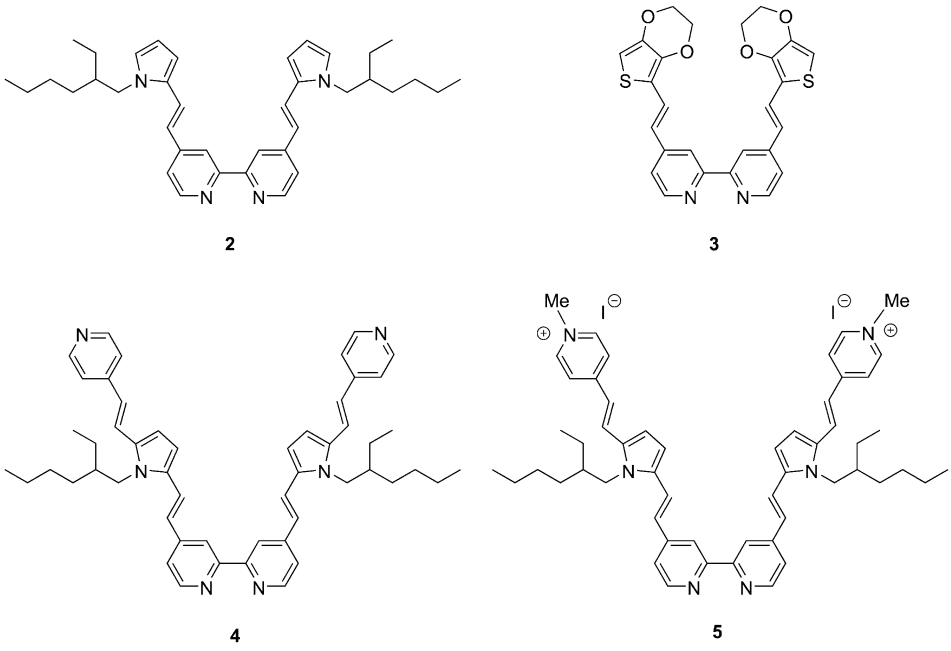
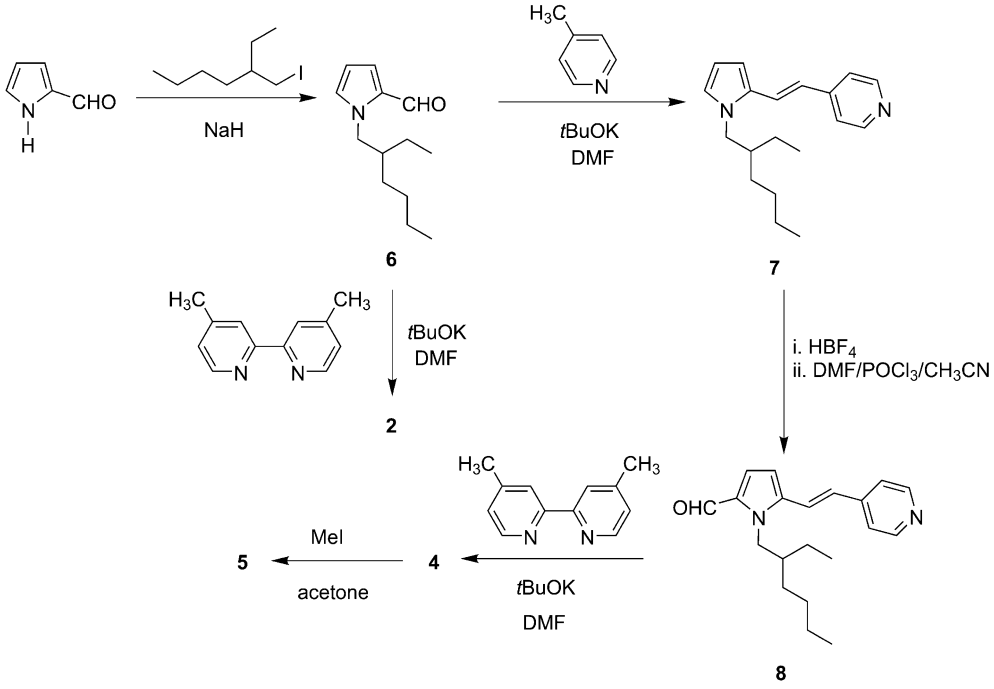


We herein report the synthesis, linear optical properties, and ab initio computations of a new class of heteroaromatic π-conjugated bpys. The two-photon-absorbing (III-order NLO) properties of the first example of the series have been recently reported by us.[14] We have adopted the following design strategy. Firstly, we have prepared bpy derivatives with two different structural symmetries: a) bpy-π-D **2** and **3** and b) bpy-π-D-π-A **4** and **5**. Secondly, we have used strong, common, heteroaromatic D and A groups: pyrrole and 3,4-ethylenedioxythiophene (EDOT) as Ds and pyridine and pyridinium as As. Ethenylic units (π) have been used as spacers.

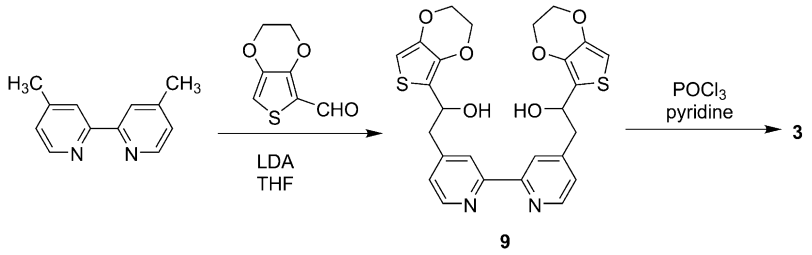
Results and Discussion

Synthesis of the Chromophores

All of the bipyridines were previously unknown in the literature, with the exception of ligand **2**, which we previously described, although it was differently functionalized



Scheme 1. Synthesis of ligands **2**, **4**, and **5**.



Scheme 2. Synthesis of ligand **3**.

at the pyrrole nitrogen.[14] The new 2-ethylhexyl derivative **2** was prepared in DMF from 4,4′-dimethyl-bpy and *N*-(2-ethylhexyl)pyrrole-2-carboxaldehyde (**6**) in the presence of potassium *tert*-butoxide (Scheme 1). Aldehyde **6** was obtained by deprotonation of pyrrole-2-carboxaldehyde with sodium hydride in DMF and alkylation with 2-ethylhexyl iodide. Condensation of the same aldehyde **6** with 4-picoline using *t*BuOK in DMF gave the 4-pyridyl-2-pyrrolylethene derivative **7**, which was protected at the pyridine nitrogen, submitted to Vilsmeier formylation, and finally deprotected to directly afford in good yields the NMR-pure aldehyde **8** as a yellow oil. Similarly to **2**, ligand **4** was then obtained from **8** through double condensation with 4,4′-dimethyl-bpy in DMF in the presence of *t*BuOK (Scheme 1). Subsequent 100% regioselective alkylation of the pyridine end-groups of the precursor tetradentate **4** with methyl iodide in dry acetone afforded the corresponding bis-*N*-methoiodide **5** in very good yields.

The same, or a similar, synthetic protocol applied to the preparation of the EDOT derivative **3** was not successful. This likely explains the fact that 4-pyridyl-EDOT-ethene derivatives are completely unknown in the literature, whereas a significant number of 4-pyridyl-2-pyrrolylethene derivatives have been previously reported by us[12–15] and others.[16] We have prepared the EDOT-conjugated bypyridine **3** in two steps as depicted in Scheme 2 via the intermediate diol **9**, which was obtained in pretty good yields by the condensation at low temperatures in THF of 4,4′-dimethyl-bpy with 3,4-(ethylenedioxy)thiophene-2-carbaldehyde[17] using lithium diisopropylamide as a base. The product was obtained as a pale yellow solid and its purity, verified by NMR, was considered sufficient for the subsequent step. Final dehydration to **3** was carried out using phosphorus oxychloride in the presence of pyridine.

Optical Characterization

The photophysical parameters (absorption and emission) of the new bipyridines **2**–**5** in DMSO are collected in Table 1. The dyes showed an intense intramolecular charge-transfer band in the visible region with absorption peaks ranging from 366 to 511 nm and molar extinction coefficients ranging from 39200 to 143500 $mol^{-1} L cm^{-1}$. The normalized absorption spectra in DMSO are shown in Figure 1.

Table 1. Absorption and emission parameters of compounds **2**–**5** in DMSO compared to literature data of the corresponding building units **10**–**12**.

	λ_{abs} [nm] [a]	$\lambda_{cut-off}$ [nm]	λ_{em} [nm]	Stokes shift [cm^{-1}] [b]	Φ_F [c]
2	377 (39200 ± 400)	438	476	5520	0.017
3	366 (63000 ± 900)	435	[d]	[d]	[d]
4	448 (133700 ± 600)	518	501	2360	0.026
5	511 (143500 ± 1500)	605	594	2730	0.036
10[e]	362[f] (21900)				
11[g]	415[f]		490[f]		
12[g]	506[f]		587[f]		

[a] Extinction coefficient ε in parentheses ($mol^{-1} L cm^{-1}$). [b] $1/\lambda_{abs} - 1/\lambda_{em}$. [c] Fluorescence quantum yield; fluorescein was used as a standard (Φ = 0.90 in 0.1 M NaOH). [d] Not fluorescent. [e] Ref.[16g]. [f] In MeOH. [g] Ref.[16b].

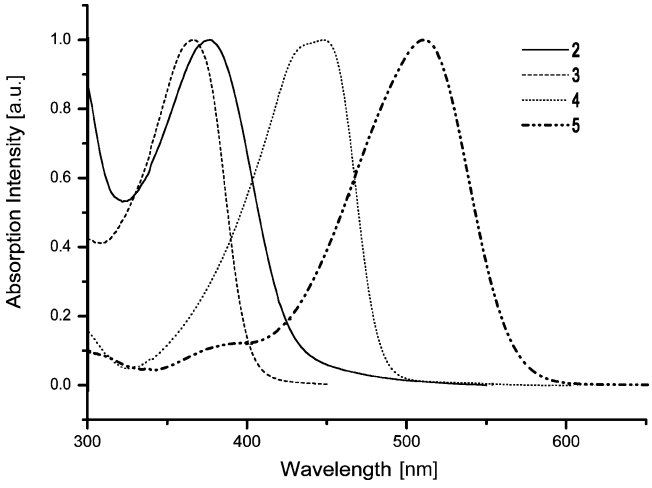
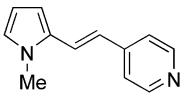


Figure 1. Absorption spectra of compounds **2**–**5** in DMSO.

The absorption properties of the bipyridines **2**, **4**, and **5** can be compared with those of the corresponding building units **10**,[16g] **11**,[16b] and **12**[16b] in order to evaluate the effects of linking two D-A heteroaromatic arms through a bipyridine core. The corresponding building unit for chromophore **3** is unknown in the literature. As expected, a bathochromic effect is present upon linking the "mono-

mers" in the bipyridine "dimers" as a consequence of the elongated π-framework. However, this effect is rather small being at most 33 nm for **4**. This can be easily explained if one considers that the two building units are not directly conjugated in the bipyridine systems.



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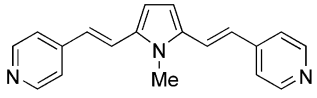

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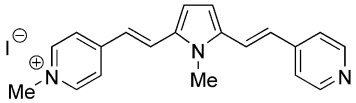

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The bipyridine dyes show a fluorescence emission with the exception of the EDOT derivative **3**, which is not fluorescent (Figure 2). The emission maxima range from 476 to 594 nm. We have previously reported the absorption (λ_{max} = 374 nm) and emission (λ_{max} = 450 nm) properties in CH_2Cl_2 of a derivative of ligand **2** carrying a tris(ethylene glycol) monomethyl ether (TEG) chain at the pyrrole nitrogen in place of the alkyl group. Since the peripheral chain does not interfere with the π-framework, differences in the two systems can be mainly ascribed to solvatochromic effects. Interestingly, a significant solvatochromic effect (26 nm) is found for the emission spectra, with a redshift upon increasing the solvent polarity, whereas no significant difference is found for the absorption peaks (377 nm for **2** in DMSO vs. 374 nm for the TEG derivative in CH_2Cl_2). The fluorescence quantum yields are modest for all the chromophores, with the bis-salt **5** being the most fluorescent dye with a 3.6% quantum yield.

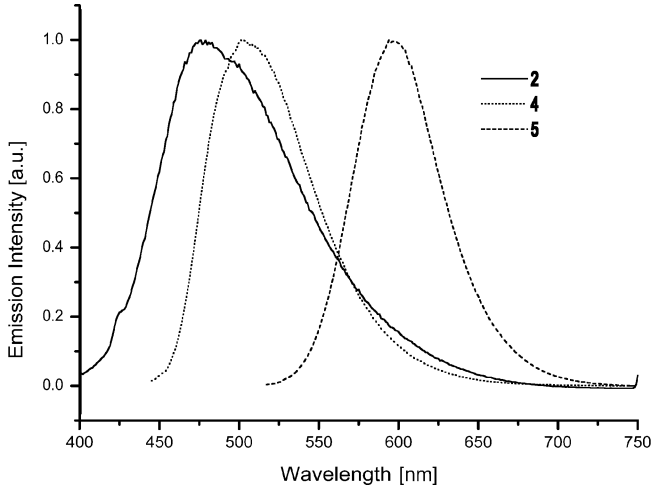

Figure 2. Emission spectra of compounds **2**, **4**, and **5** in DMSO.

Computational Investigation

To gain insight into the structural, electronic, and optical properties of the investigated ligands, we performed DFT and Time-Dependent DFT (TDDFT) calculations on systems **2**–**5**. We optimized the molecular structures of the four systems without any symmetry constraints using the B3LYP exchange-correlation functional and a 6-31G* basis set. Using the same computational setup, we performed TDDFT calculations of the singlet-singlet excited states at the optimized geometries, in order to simulate the optical absorption spectrum of the investigated systems. All of the calculations have been performed by the GAUSSIAN 03 program package.[18] Geometry optimizations were performed considering both a *cisoid* and a *transoid* arrangement of the bipyridines. In all cases, the *transoid* arrangement was found to be favored over the *cisoid* one. The *transoid* form was calculated to be more stable by 3.8–10.0 kcal mol^{-1} over the *cisoid* form; the highest difference was found for the bis-salt **5**, likely due to the stronger electrostatic repulsion between the two charged arms of the ligand. Optimized geometrical parameters for the investigated species are rather similar and will not be discussed in detail. Instead, our discussion will follow on the electronic and optical properties.

A schematic representation of the molecular orbitals for the more stable *transoid* forms of **2**–**5** is shown in Figure 3. Since species **5** is twice positively charged, we aligned the energy of its HOMO to that of the parent species **4**, discussing in this case only energy differences. On the other hand, a direct comparison is possible for species **2**–**4**, which have the same total charge. As can be seen in Figure 3, the nature of the HOMO and LUMO is the same in molecules **2**–**4**. In particular, the HOMOs are a couple of degenerate π orbitals differing only in their phase, while the LUMOs are the corresponding π* counterparts, with sizeable contributions from the C–C bond connecting the two pyridine moieties. The LUMO+1 (Figure 4) is a π* molecular orbital with a different localization compared to that of the LUMO. The HOMO of **5** is similar to that of **2**–**4**, whereas its LUMO is essentially localized on the outer molecular region; the LUMO+2 in **5** corresponds to the LUMO in **2**–**4**. The bpy-π-D ligands **2** and **3** have similar properties, although a consistent stabilization of both the occupied and unoccupied orbitals is calculated on going from **2** to **3**. The HOMO of **3** is stabilized by 0.25 eV, whereas its LUMO is stabilized by 0.13 eV, resulting in an increase of the HOMO-LUMO gap in **3** by 0.12 eV compared to that of **2**. The larger HOMO-LUMO gap of **3** is directly reflected in its lowest excitation energy, which is higher by 0.11 eV compared to that of **2**. Interestingly, the extended π-conjugation in **4** does not substantially alter the position of the HOMO with respect to **2**. In contrast, a drastic LUMO stabilization (0.58 eV) is calculated on going from **2** to **4**. A significant reduction of the HOMO-LUMO gap (2.91 vs. 3.50 eV) and a concomitant variation of the lowest excitation energy (2.71 vs. 3.20 eV) is therefore computed for **4** compared to **2**. The quaternarization of the terminal pyridine rings in **5**

leads to a further decrease of the HOMO–LUMO gap and of the lowest excited state, in agreement with the stronger electron-withdrawing capacity of the positively charged pyridinium substituents.

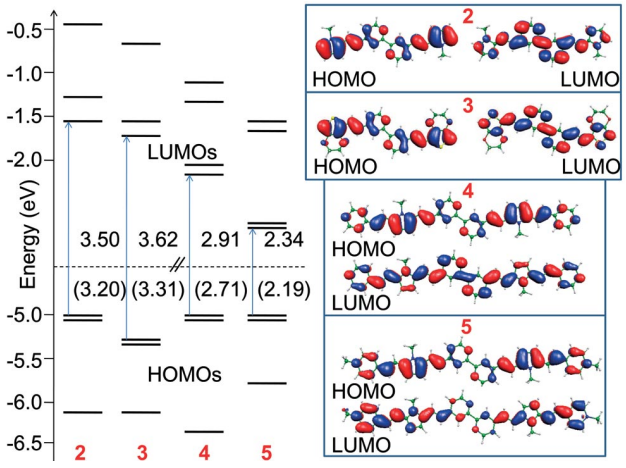

Figure 3. Schematic representation of the molecular orbitals, HOMO–LUMO gaps [eV], lowest TDDFT excitation energies (eV, values in parenthesis), and isodensity plots of HOMO and LUMO for chromophores **2**–**5**.

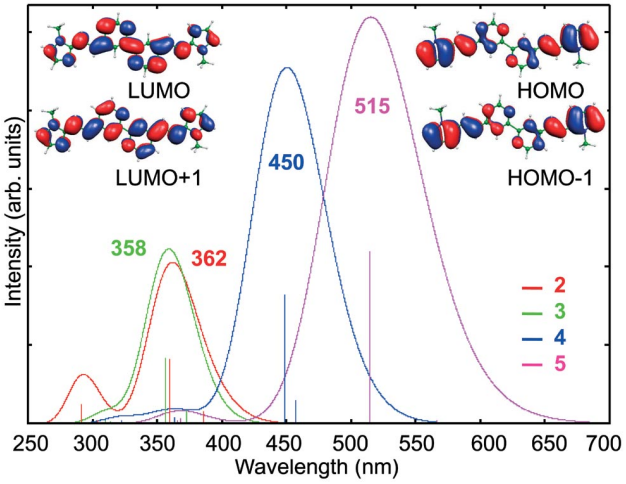

Figure 4. Calculated absorption spectra and maxima [nm] for chromophores **2**–**5**. The absorption spectra were obtained by a gaussian convolution centered on excitation energies, with a σ = 0.17 eV. HOMO-1, HOMO, LUMO, and LUMO+1 orbitals are shown for molecule **2**.

Figure 4 shows the calculated TDDFT absorption spectra of **2**–**5**. The agreement between calculated and experimental absorption maxima is excellent (362 vs. 377 nm, 358 vs. 366 nm, 450 vs. 448 nm, and 515 vs. 511 nm for **2**–**5**, respectively), with a maximum deviation of 0.14 eV calculated for **2**. The relative absorption maxima intensities for **3**–**5** are accurately reproduced by the theoretical approach. Indeed, a value of 2.03 is computed for the relative absorption maximum intensity of molecule **4** with respect to molecule **3**, to be compared with an experimental extinction coefficient ratio of 2.13 (Table 1). Similarly, the computed relative intensity of 2.32 of the absorption peak of **5** with respect to that of **3** can be compared with an experimental value of 2.29. On the other hand, we calculated almost the same intensity for the absorption maxima of **2** and **3**, while a factor of ca. 1.5 was experimentally found.

The analysis of the TDDFT eigenvectors allows us to assign the nature of the excited states responsible for the absorption spectra. The lowest transition, corresponding to the HOMO → LUMO excitation, is symmetry forbidden in molecules **2**–**4** and does not contribute to their absorption spectrum. This dark excited state is followed by an almost degenerate, rather intense (f = 0.30, 0.33, and 0.60 for **2**–**4**, respectively) transition involving the HOMO-1 → LUMO excitation. The third-excited state, involving a HOMO → LUMO+1 transition, dominates the absorption spectrum thanks to its strong intensity (f = 1.64, 1.67, and 3.30 for **2**–**4**, respectively). A different pattern of excited states is computed for bipyridine **5**. The two almost degenerate sets of HOMOs and LUMOs give rise to four transitions: two degenerate transitions at 566 nm (f = 0.0 and 0.1) and two transitions at 512 and 479 nm (f = 3.39 and 0.0, respectively). The absorption spectrum is therefore dominated by the single very intense transition at 512 nm, constituted by a combination (0.44 and 0.25, respectively) of HOMO-1 → LUMO+1-HOMO → LUMO orbital excitations with similar coefficients.

Conclusions

In this study a combination of organic synthesis, absorption and emission spectroscopy, and ab initio computations have been applied to the design, preparation, and characterization of a new class of 4,4′-π-conjugated bpys. Considering the great importance of bipyridines in many areas of chemistry and materials science we believe that this work can give a significant contribution to the field by introducing the first example of D and A heteroaromatic-substituted bipyridines. A judicious combination of π-excessive and π-deficient heteroaromatic groups with bipyridine frameworks can be successfully exploited to access a new series of nitrogen ligands with tunable optical and electronic properties.

Indeed, the new heteroaromatic bipyridines have absorption and emission spectra ranging over a broad interval of the visible spectrum. Their energy levels and molecular orbitals can be efficiently tuned as well. In particular, computed HOMO and LUMO levels closely depend on the presence and strength of heteroaromatic D and A substituents. Similarly, the nature of the main molecular orbitals is affected by the type of heteroaromatic substitution in the ligands. The computational investigation of the energy levels and molecular orbitals is validated by the excellent qualitative and quantitative agreement with the experimental optical measurements.

In conclusion, we have presented the first series of heteroaromatic 4,4′-π-conjugated bpys with tunable optical and energetic properties which, in turn, can be properly exploited to optimize material properties. The investigation of

the members of this class as components in materials for NLO (two-photon absorption) and dye-sensitized solar cells is in progress.

Experimental Section

General: NMR spectra were recorded with a Bruker AMX-500 instrument operating at 500.13 (^{1}H) and 125.77 MHz (^{13}C). Assignments of ^{13}C resonances were based on ^{1}H-^{13}C HETCOR and long-range HETCOR experiments and literature data.[16g] High-resolution mass spectra (HRMS) obtained by Electrospray ionization (ESI) were recorded using a Bruker Daltonics ICR-FTMS APEX II spectrometer. HRMS for compound **3** was provided by the Washington University Mass Spectrometry Resource (NIH National Center for Research Resources P41RR0954). Flash Chromatography was performed with Sigma–Aldrich silica gel 60 (230–400 mesh). All reagents were obtained from commercial suppliers and used without further purification. Solvents were generally dried and distilled prior to use. Anhydrous solvents were purchased from Aldrich. Extracts were dried with Na_2SO_4. Melting points are uncorrected.

1-(2-Ethylhexyl)-1*H*-pyrrole-2-carbaldehyde (6): A solution of pyrrole-2-carbaldehyde (571 mg, 6.00 mmol) in DMF (5 mL) was added dropwise to a suspension of NaH (60% dispersion in mineral oil, 265 mg, 6.6 mmol) in the same solvent (3 mL). 2-Ethylhexyl iodide (1.08 mL, 1.44 g, 6.00 mmol) in DMF (3 mL) was added dropwise, and the resulting mixture was stirred at 70 °C for 24 h. Et_2O (300 mL) and brine (300 mL) were added, and the layers were separated. The organic layer was washed with brine (3 × 300 mL), dried, and the solvent was evaporated to dryness. The residue was purified by flash chromatography (petroleum ether/Et_2O, 14:1), yielding the practically pure product as a colorless oil (535 mg, 2.58 mmol, 43%), which was used without further purification in the next step. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.50 (s, 1 H), 7.28 (broad s, 1 H), 7.02 (dd, J = 4.0, 1.7 Hz, 1 H), 6.23 (dd, J = 4.0, 2.4 Hz, 1 H), 4.22–4.13 (m, 2 H), 1.72 (sept, J = 6.0 Hz, 1 H), 1.28–1.08 (m, 8 H), 0.83 (t, J = 7.1 Hz, 3 H), 0.80 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 179.63 (1 C, CHO), 133.18 (1 C, C-5 of pyrrole ring), 131.66 (1 C, C-2 of pyrrole ring), 125.08 (1 C, C-3 of pyrrole ring), 109.66 (1 C, C-4 of pyrrole ring), 52.20 (1 C, α-CH_2 of alkyl chain), 40.15 (1C, β-CH of alkyl chain, partially covered by solvent peak), 30.02 (1 C, CH_2 of alkyl chain), 28.22 (1 C, CH_2 of alkyl chain), 23.44 (1 C, CH_2 of alkyl chain), 22.92 (1 C, CH_2 of alkyl chain), 14.30 (1 C, CH_3 of alkyl chain), 10.71 (1 C, CH_3 of alkyl chain) ppm.

4,4′-Bis{(*E*)-2-[*N*-(2-ethylhexyl)pyrrol-2-yl]vinyl}-2,2′-bipyridine (2): *t*BuOK (260 mg, 2.12 mmol) and **6** (400 mg, 1.93 mmol) were added to a solution of 4,4′-dimethyl-2,2′-bipyridine (178 mg, 0.966 mmol) in anhydrous DMF (8 mL), and the resulting mixture was stirred for 1.5 h. AcOEt (150 mL) and brine (150 mL) were added, and the layers were separated. The organic layer was washed with brine (2 × 150 mL), dried, and the solvent was evaporated to dryness to leave a residue, which was submitted to flash chromatography (hexanes/AcOEt/MeOH/NH_3, 8:2:0.1:0.05), yielding **2** as an orange oil (445 mg, 0.791 mmol, 82%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.58 (d, J = 5.1 Hz, 2 H), 8.43 (s, 2 H), 7.60 (d, J = 4.5 Hz, 2 H), 7.47 (d, J = 16.0 Hz, 2 H), 6.99 (d, J = 16.0 Hz, 2 H), 6.89 (s, 2 H), 6.67 (d, J = 2.1 Hz, 2 H), 6.12 (t, J = 2.6 Hz, 2 H), 4.02 (dd, ^2J = 14.4, ^3J = 7.4 Hz, 2 H), 3.98 (dd, ^2J = 14.4, ^3J = 7.9 Hz, 2 H), 1.72–1.60 (m, 2 H), 1.35–1.10 (m, 16 H), 0.85 (t, J = 7.3 Hz, 6 H), 0.82 (t, J = 6.7 Hz, 6 H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 156.35 (2 C, C-2 and C-2′ of bipyridine ring), 149.81 (2 C, C-6 and C-6′ of bipyridine ring), 146.64 (2 C, C-4 and C-4′ of bipyridine ring), 130.62 (2 C, C-2 of pyrrole rings), 125.57 (2 C, C-5 of pyrrole rings), 122.56 (2 C, α-CH of ethene bridge to bipyridine ring), 121.97 (2 C, β-CH of ethene bridge to bipyridine ring), 120.37 (2 C, C-5 and C-5′ of bipyridine ring), 117.78 (2 C, C-3 and C-3′ of bipyridine ring), 108.98 (2 C, C-3 or C-4 of pyrrole rings), 108.88 (2 C, C-3 or C-4 of pyrrole rings), 50.29 (2 C, α-CH_2 of alkyl chains), 41.43 (2 C, β-CH of alkyl chains), 30.36 (2 C, CH_2 of alkyl chains), 28.44 (2 C, CH_2 of alkyl chains), 23.83 (2 C, CH_2 of alkyl chains), 22.93 (2 C, CH_2 of alkyl chains), 14.28 (2 C, CH_3 of alkyl chains), 10.99 (2 C, CH_3 of alkyl chains) ppm. HRMS-ESI: m/z calcd. for [M + H]$^+$ 563.41082, found 563.41006; calcd. for [M + Na]$^+$ 585.39277, found 585.39146. $C_{38}H_{50}N_4 \cdot 0.5H_2O$ (571.84): calcd. C 79.81, H 8.99, N 9.80; found: C 79.83, H 8.75, N 9.67.

4,4′-Bis[2-hydroxy-2-(3,4-ethylenedioxythien-2-yl)ethyl]-2,2′-bipyridine (9): LDA (1.8 mL, 1.8 M in hexane, 3.24 mmol) was added dropwise to a stirred solution of 4,4′-dimethyl-2,2′-bipyridine (270 mg, 1.47 mmol) in THF (15 mL) at 0 °C. After 10 min, a solution of 3,4-(ethylenedioxy)thiophene-2-carbaldeyde[17] (500 mg, 2.94 mmol) in THF (15 mL) was added dropwise, and the resulting mixture was warmed up to room temperature and stirred for 1.5 h. AcOEt and brine were added to the reaction mixture. The organic layer was separated, washed to neutrality, dried, and the solvent was evaporated to dryness to give the product (440 mg, 0.84 mmol, 57%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.56 (d, J = 4.8 Hz, 2 H), 8.32 (s, 2 H), 7.20 (d, J = 5.0 Hz, 2 H), 6.28 (s, 2 H), 5.29 (t, J = 6.7 Hz, 2 H), 4.20–4.10 (m, 8 H), 3.22 (d, J = 6.8 Hz, 4 H) ppm.

4,4′-Bis[(*E*)-2-(3,4-ethylenedioxythien-2-yl)vinyl]-2,2′-bipyridine (3): Diol **9** (200 mg, 0.38 mmol) was dissolved in pyridine (4 mL). Freshly distilled $POCl_3$ (87 μL, 141 mg, 0.92 mmol) was added dropwise at 0 °C, and the resulting mixture was stirred for 10 min. AcOEt (50 mL) and H_2O (50 mL) were added to the reaction mixture, and the organic layer was separated, washed with H_2O (3 × 50 mL), dried, and the solvent was evaporated to dryness. Flash column chromatography of the residue (silica gel, AcOEt) afforded **1** as a yellow solid (73 mg, 0.15 mmol, 40%). M.p. > 250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.64 (d, J = 5.1 Hz, 2 H), 8.48 (s, 2 H), 7.50 (d, J = 16.2 Hz, 2 H), 7.36 (dd, J = 5.1, J = 1.5 Hz, 2 H), 6.93 (d, J = 16.2 Hz, 2 H), 6.35 (s, 2 H), 4.36–4.32 (m, 4 H), 4.29–4.24 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.17 (2 C, C-2 and C-2′ of bipyridine ring), 149.28 (2 C, C-6 and C-6′ of bipyridine ring), 146.11 (2 C, C-4 and C-4′ of bipyridine ring), 142.07 (2 C, C-4 of EDOT rings), 140.74 (2 C, C-3 of EDOT rings), 123.41 (2 C, α-CH of ethene bridge to bipyridine ring), 122.99 (2 C, β-CH of ethene bridge to bipyridine ring), 120.50 (2 C, C-5 and C-5′ of bipyridine ring), 118.03 (2 C, C-3 and C-3′ of bipyridine ring), 116.16 (2 C, C-2 of EDOT rings), 99.86 (2 C, C-5 of EDOT rings), 64.93 (2 C, OCH_2 of EDOT rings), 64.67 (2 C, OCH_2 of EDOT rings) ppm. HRMS-ESI: m/z calcd. for [M + H]$^+$ 489.0943, found 489.0936. $C_{26}H_{20}N_2O_4S_2 \cdot H_2O$ (506.59): calcd. C 61.64, H 4.38, N 5.53; found: C 61.49, H 4.13, N 5.46.

(*E*)-1-(Pyridin-4-yl)-2-[*N*-(2-ethylhexyl)pyrrol-2-yl]ethene (7): 4-Picoline (0.847 μL, 8.7 mmol) and *t*BuOK (1.06 g, 8.7 mmol) were added to a solution of **6** (1.50 g, 7.2 mmol) in DMF (5 mL). After stirring for 2 h, the reaction mixture was poured into ice-cold water (250 mL), and AcOEt (250 mL) was added. The organic layer was separated, washed with brine (2 × 200 mL), dried, and concentrated under reduced pressure to leave a residue which was submitted to flash chromatography (petroleum ether/AcOEt, 65:35), yielding the pure compound as a colorless oil (1.35 g, 4.8 mmol, 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.54 (d, J = 6.2 Hz, 2 H), 7.30 (d,

J = 6.2 Hz, 2 H), 7.20 (d, J = 16.0 Hz, 1 H), 6.78 (d, J = 16.0 Hz, 1 H), 6.72 (t, J = 2.1 Hz, 1 H), 6.63 (dd, J = 3.7, 1.5 Hz, 1 H), 6.21 (t, J = 3.1 Hz, 1 H), 3.92 (dd, ^2J = 14.3, ^3J = 7.1 Hz, 1 H), 3.87 (dd, ^2J = 14.3, ^3J = 6.7 Hz, 1 H), 1.75 (sept, J = 6.0 Hz, 1 H), 1.40–1.20 (m, 8 H), 0.95 (t, J = 7.4 Hz, 3 H), 0.92 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.62 (2 C, C-2 and C-6 of pyridine ring), 145.79 (1 C, C-4 of pyridine ring), 130.35 (1 C, C-2 of pyrrole ring), 124.87 (1 C, C-5 of pyrrole ring), 121.88 (1 C, β-CH of ethene bridge to pyridine ring), 121.68 (1 C, α-CH of ethene bridge to pyridine ring), 120.20 (2 C, C-3 and C-5 of pyridine ring), 108.71 (1 C, C-3 or C-4 of pyrrole ring), 108.56 (1 C, C-3 or C-4 of pyrrole ring), 50.97 (1 C, α-CH_2 of alkyl chain), 41.41 (1 C, β-CH of alkyl chain), 30.62 (1 C, CH_2 of alkyl chain), 28.67 (1 C, CH_2 of alkyl chain), 23.96 (1 C, CH_2 of alkyl chain), 22.97 (1 C, CH_2 of alkyl chain), 14.01 (1 C, CH_3 of alkyl chain), 10.69 (1 C, CH_3 of alkyl chain) ppm.

(*E*)-1-(Pyridin-4-yl)-2-[5-formyl-*N*-(2-ethylhexyl)pyrrol-2-yl]ethene (8): Aqueous HBF_4 (8 M, 0.6 mL, 4.8 mmol) was added dropwise to a solution of **7** (1.30 g, 4.60 mmol) in absolute ethanol (35 mL), and the resulting mixture was stirred for 1.5 h. The solid tetrafluoborate salt of protonated 1-(pyridin-4-yl)-2-[*N*-(2-ethylhexyl)pyrrol-2-yl]ethene was filtered off, washed with cold EtOH, dried under vacuum, and used without further purification in the next step. Anhydrous DMF (0.5 mL, 6.5 mmol) was added dropwise to freshly distilled $POCl_3$ (0.6 mL, 6.5 mmol) at 0 °C under nitrogen. The resulting solution was stirred at 0 °C for 15 min and a glassy white solid was obtained, which was taken up with anhydrous CH_3CN (10 mL). A solution of the tetrafluoborate salt of protonated 1-(pyridin-4-yl)-2-[*N*-(2-ethylhexyl)pyrrol-2-yl]ethene in anhydrous CH_3CN (30 mL) was added dropwise, and the resulting mixture was refluxed for 2 h. The mixture was then poured into aqueous K_2CO_3 (10%, 300 mL) and stirred for 1 h. After adding AcOEt (300 mL), the organic layer was separated, washed with brine (3 × 200 mL), dried, and the solvent was evaporated to dryness. The residue was submitted to flash chromatography (petroleum ether/AcOEt, 1:1) to afford the pure compound as a yellow oil (0.943 g, 3.04 mmol, 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.55 (s, 1 H), 8.62 (d, J = 6.1 Hz, 2 H), 7.37 (d, J = 6.1 Hz, 2 H), 7.22 (d, J = 16.0 Hz, 1 H), 7.05 (d, J = 16.0 Hz, 1 H), 6.97 (d, J = 4.3 Hz, 1 H), 6.68 (d, J = 4.3 Hz, 1 H), 4.46 (dd, ^2J = 14.1, ^3J = 4.4 Hz, 1 H), 4.43 (dd, ^2J = 14.4, ^3J = 4.1 Hz, 1 H), 1.77 (sept, J = 6.4 Hz, 1 H), 1.40–1.20 (m, 8 H), 0.92 (t, J = 7.4 Hz, 3 H), 0.88 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 179.15 (1 C, CHO), 150.00 (2 C, C-2 and C-6 of pyridine ring), 144.27 (1 C, C-4 of pyridine ring), 139.77 (1 C, C-2 or C-5 of pyrrole ring), 133.42 (1 C, C-2 or C-5 of pyrrole ring), 128.96 (1 C, α-CH of ethene bridge to pyridine ring), 125.05 (1 C, C-3 or C-4 of pyrrole ring), 120.71 (2 C, C-3 and C-5 of pyridine ring), 120.35 (1 C, β-CH of ethene bridge to pyridine ring), 109.09 (1 C, C-3 or C-4 of pyrrole ring), 48.94 (1 C, α-CH_2 of alkyl chain), 41.55 (1 C, β-CH of alkyl chain), 30.38 (1 C, CH_2 of alkyl chain), 28.63 (1 C, CH_2 of alkyl chain), 23.79 (1 C, CH_2 of alkyl chain), 22.98 (1 C, CH_2 of alkyl chain), 13.97 (1 C, CH_3 of alkyl chain), 10.93 (1 C, CH_3 of alkyl chain) ppm.

4,4′-Bis((*E*)-2-{1-(2-ethylhexyl)-5-[(*E*)-2-(pyridin-4-yl)vinyl]pyrrol-2-yl}vinyl)-2,2′-bipyridine (4): 4,4′-Dimethyl-2,2′-bipyridine (74 mg, 0.40 mmol) and *t*BuOK (108 mg, 0.88 mmol) were added to a solution of **8** (250 mg, 0.80 mmol) in anhydrous DMF (2 mL), and the resulting mixture was stirred for 2 h. AcOEt (50 mL) and brine (50 mL) were added, and the layers were separated. The organic layer was washed with brine (2 × 50 mL) and dried, and the solvent was removed under reduced pressure to give a residue which was purified by flash chromatography (AcOEt/MeOH/aqueous ammonium hydroxide 25:0.1:0.05) to yield **4** as an orange solid (120 mg, 0.16 mmol, 20%). M.p. 167–168 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (d, J = 5.1 Hz, 2 H), 8.57 (d, J = 6.0 Hz, 4 H), 8.47 (s, 2 H), 7.38–7.27 (m, 8 H), 7.22 (d, J = 15.9 Hz, 2 H), 6.99 (d, J = 15.9 Hz, 2 H), 6.86 (d, J = 15.9 Hz, 2 H), 6.73 (s, 4 H), 4.07 (dd, ^2J = 14.9, ^3J = 7.3 Hz, 2 H), 4.02 (dd, ^2J = 15.1, ^3J = 7.5 Hz, 2 H), 1.86–1.69 (m, 2 H), 1.46–1.24 (m, 16 H), 0.98 (t, J = 7.3 Hz, 6 H), 0.89 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.63 (2 C, C-2 and C-2′ of bipyridine ring), 150.20 (4 C, C-2 and C-6 of pyridine rings), 149.47 (2 C, C-6 and C-6′ of bipyridine ring), 146.03 (2 C, C-4 and C-4′ of bipyridine ring), 145.00 (2 C, C-4 of pyridine rings), 133.75 (2 C, pyrrole rings α-C close to bipyridine), 133.51 (2 C, pyrrole rings α-C close to pyridine), 124.02 (2 C, α-CH of ethene bridge to bipyridine ring), 123.47 (2 C, α-CH of ethene bridge to pyridine rings), 121.05 (2 C, β-CH of ethene bridge to bipyridine ring), 120.97 (2 C, β-CH of ethene bridge to pyridine ring), 120.20 (4 C, C-3 and C-5 of pyridine rings), 120.12 (2 C, C-5 and C-5′ of bipyridine ring), 117.98 (2 C, C-3 and C-3′ of bipyridine ring), 109.56 (2 C, pyrrole rings β-C), 109.54 (2 C, pyrrole rings β-C), 47.37 (2 C, α-CH_2 of alkyl chains), 41.96 (2 C, β-CH of alkyl chains), 30.79 (2 C, CH_2 of alkyl chains), 28.87 (2 C, CH_2 of alkyl chains), 24.24 (2 C, CH_2 of alkyl chains), 23.00 (2 C, CH_2 of alkyl chains), 13.99 (2 C, CH_3 of alkyl chains), 11.17 (2 C, CH_3 of alkyl chains) ppm. HRMS-ESI: m/z calcd. for $[M + H]^+$ 769.49522, found 769.49384; calcd. for $[M + Na]^+$ 791.47717, found 791.47520. $C_{52}H_{60}N_6 \cdot 2H_2O$ (805.10): calcd. C 77.57, H 8.01, N 10.44; found C 77.58, H 7.62, N 10.26.

4,4′-Bis((*E*)-2-{1-(2-ethylhexyl)-5-[(*E*)-2-(4-*N*-methylpyridinium)-vinyl]pyrrol-2-yl}vinyl)-2,2′-bipyridine diiodide (5): Methyl iodide (81 μL, 1.30 mmol) was added to a stirred solution of **4** (50 mg, 0.065 mmol) in dry acetone (5 mL). The color of the reaction turned immediately from orange to dark red and the resulting mixture was refluxed for 3.5 h. After standing overnight at room temperature, the product **4** formed as a dark precipitate (60 mg, 0.057 mmol, 88%) which was collected and washed with cold acetone. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.70 (d, J = 7.0 Hz, 4 H), 8.67 (d, J = 5.1 Hz, 2 H), 8.52 (s, 2 H), 8.11 (d, J = 6.8 Hz, 4 H), 7.96 (d, J = 15.4 Hz, 2 H), 7.70 (d, J = 3.9 Hz, 2 H), 7.61 (d, J = 15.9 Hz, 2 H), 7.30 (d, J = 15.9 Hz, 2 H), 7.20 (d, J = 15.5 Hz, 2 H), 7.09 (d, J = 4.1 Hz, 2 H), 7.00 (d, J = 4.4 Hz, 2 H), 4.39 (d, J = 7.4 Hz, 4 H), 4.19 (s, 6 H), 1.65–1.55 (m, 2 H), 1.38–1.14 (m, 16 H), 0.87 (t, J = 7.5 Hz, 6 H), 0.79 (t, J = 7.3 Hz, 6 H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 156.45 (2 C, C-2 and C-2′ of bipyridine ring), 153.36 (2 C, C-4 of pyridinium rings), 150.05 (2 C, C-6 and C-6′ of bipyridine ring), 146.07 (2 C, C-4 and C-4′ of bipyridine ring), 144.86 (4 C, C-2 and C-6 of pyridinium rings), 136.97 (2 C, C-2 or C-5 of pyrrole rings), 133.80 (2 C, C-2 or C-5 of pyrrole rings), 129.32 (2 C, β-CH of ethene bridge to pyridinium rings), 126.17 (2 C, α-CH of ethene bridge to pyridinium rings), 122.64 (4 C, C-3 and C-5 of pyridinium rings), 121.86 (2 C, β-CH of ethene bridge to bipyridine ring), 120.78 (2 C, 5-C and 5′-C of bipyridine ring), 119.29 (2 C, α-CH of ethene bridge to bipyridine ring), 118.34 (2 C, C-3 and C-3′ of bipyridine ring), 113.61 (2 C, C-3 or C-4 of pyrrole rings), 111.57 (2 C, C-3 or C-4 of pyrrole rings), 46.88 (2 C, N-CH_3 of pyridinium rings), 46.74 (2 C, α-CH_2 of alkyl chains), 42.11 (2 C, β-CH of alkyl chains), 30.28 (2 C, CH_2 of alkyl chains), 28.42 (2 C, CH_2 of alkyl chains), 23.86 (2 C, CH_2 of alkyl chains), 22.96 (2 C, CH_2 of alkyl chains), 14.24 (2 C, CH_3 of alkyl chains), 11.34 (2 C, CH_3 of alkyl chains) ppm. HRMS-ESI: m/z calcd. for $[M]^{2+}$ 399.26690, found 399.26639; calcd. for $[M - I]^+$ 925.43882, found 925.44097. $C_{54}H_{66}I_2N_6 \cdot 2H_2O$ (1088.98): calcd. C 59.56, H 6.48, N 7.72; found C 59.98, H 6.77, N 7.50.

Computations: All of the calculations were performed in vacuo using the B3LYP exchange-correlation functional, together with a 6-31G* basis set. TDDFT calculations have been performed using the same computational setup. The opt = loose option was used to speed up geometry optimizations. The conver = 2 option was used to regulate the convergence of the solution of TDDFT equations.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra (full and aromatic region) of compounds **2**–**5**.

Acknowledgments

Research was supported by Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM) (PRISMA 2005) and Ministero dell'Istruzione, dell'Università e della Ricerca (PRIN 2006031511 and FIRB RBNE033KMA). F. D. A. wishes to thank INSTM (PRISMA 2007) and Consiglio Nazionale delle Ricerche (CNR-PROMO 2006) for financial support.

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Received: July 13, 2008
Published Online: September 10, 2008

