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LETTERS

Syntheses and photophysical properties of rigid-rod conjugated compounds based on *N*-7-azaindole and 2,2′-dipyridylamine

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Abstract—Rigid-rod conjugated compounds based on *N*-7-azaindole and 2,2′-dipyridylamine functional groups have been synthesized as potential compounds for molecular electronic devices via Pd-mediated Sonogashira couplings. Their photoluminescent properties have been investigated. © 2002 Elsevier Science Ltd. All rights reserved.

N-Donor chelated organic compounds based on 7-azaindole and 2,2′-dipyridylamine have recently attracted considerable interest because of their applications in organic light-emitting-devices (OLEDs), their coordination chemistry of main groups and/or transition metals as well as potential building blocks for supramolecular nanoengineering.[1] A variety of studies on π-conjugated organic molecular rods with rigid entities such as carbon–carbon triple bonds have been shown to have unique physical and chemical properties.[2] For example, organic oligomers and polymers of bipyridines, phenylenes, and phenylamines incorporating ethynylene or alternating ethynylene groups with pyridine and phenylenes have been demonstrated as useful new materials for electronic and photonic conductors[3] and for nonlinear optics.[4] In particular, nano scale conjugated rods built from phenylene–ethynylene and phenanthrenes central units have been designed for two-photon-excited fluorophores[5a–b] and a series of triarylamine derivatives, which are linked by ethynylene, butadiyne, 1,4-diethynylbenzene, have been prepared as model compounds to understand electron-transfer processes in biological systems.[5c,d] During our ongoing investigation of luminescent organic compounds, we have observed that deprotonated 7-azaindole, 2,2′-dipyridylamine and their derivatives are efficient blue emitters when irradiated by UV light.[6] Our interest in the synthesis of highly conjugated organic spacers containing 7-azaindole or 2,2′-dipyridylamine functional groups, which can provide binding sites for metal ions, has prompted us to investigate the syntheses of their derivatives, linked by internal alkyne units via Pd-mediated Sonogashira coupling.[7] Herein, we report the syntheses, and photophysical properties of rigid molecular rods based on 7-azaindole and 2,2′-dipyridylamine.

Compounds **1** and **2** were prepared from the reaction of excess 1,4-dibromobenzene with 7-azaindole and 2,2-dipyridylamine through the Ullman condensation,[8] using K_2CO_3/KOH, and $CuSO_4$ (as a base and catalyst, respectively), in moderate yields (43–60%). The significant factors in these reactions are the reaction temperatures and times. If the reaction temperature is not sufficiently high, no reaction occurs. If the reaction time is longer than 6 h, 1,4-disubstituted compounds and unidentified metal complexes are obtained as major components. The optimum reaction conditions are described in Scheme 1. The introduction of an ethynyl unit between 7-azaindolylphenyl or 2,2′-dipyridylaminophenyl functional moieties was carried out by using a sequence of Pd-mediated Sonogashira coupling reactions of trimethylsilylacetylene with the corresponding bromoarenes, as shown in Scheme 1, producing compounds **3** and **4**, respectively. Further coupling of **3** and **4** with compounds **1** or **2** produced compounds **5**, **6** and **7**. In addition, the oxidative coupling reaction of compound **4** in the presence of oxygen and Cu(I) produced compound **8** in good yield (88%). All compounds are soluble in common organic solvents except hexane.

The syntheses of compounds **9** and **10** were achieved by using two different methods (Scheme 2). One method involves the reaction of a 1,4-dibromobenzene or 4,4′-dibromobiphenyl with compound **4**. The other method involves the reaction of 1,4-diethynylbenzene or 4,4′-diethynylbiphenyl with compound **2**. Compound **9** was

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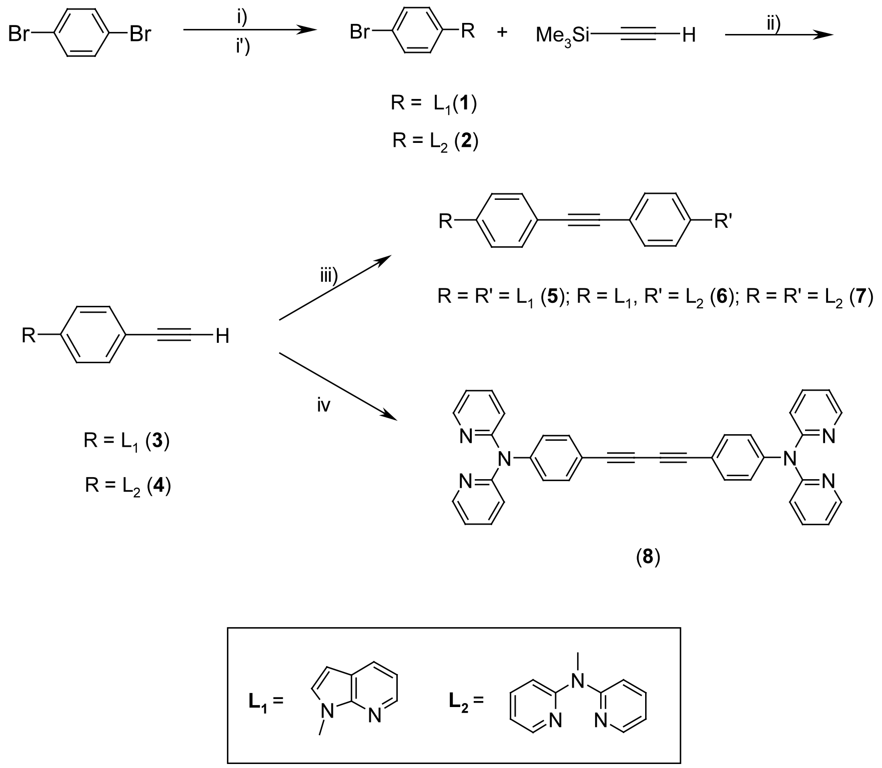
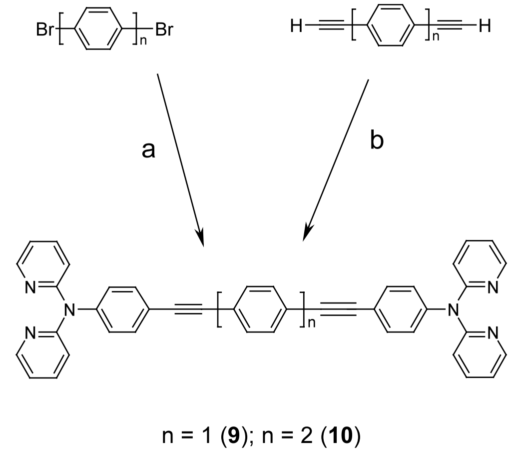


Scheme 1. *Reagents and conditions*: (i) *N*-7-Azaindole, K_2CO_3 (1 equiv.), $CuSO_4$ (5 mol%), 210–220°C, 6 h, 43%. (i′) 2,2′-Dipyridylamine, KOH (1.5 equiv.), $CuSO_4$ (5 mol%), 210–220°C, 4 h, 60%. (ii) $Pd(PPh_3)_4$, CuI, NEt_3, 80–100°C, 12 h (80–86%). KOH (excess), MeOH/THF (2:1), 20 min (93–95%). (iii) **1** or **2**, $Pd(PPh_3)_4$, CuI, NEt_3, 80–100°C, 24 h (60–75%). (iv) CuCl, pyridine, O_2, rt, 24 h (88%).



Scheme 2. *Reagents and conditions*: (a) **4**, $Pd(PPh_3)_4$, CuI, NEt_3, 80–100°C, 24 h, yield 65%. (b) **2**, $Pd(PPh_3)_4$, CuI, NEt_3, 80–100°C, 24 h, yield 52%.

prepared by both approaches in high yield. However, in the case of compound **10**, the second approach was preferable, because compound **5** was also isolated as a by-product with significant yield (28–33%) by using the first approach. The structures of all compounds were confirmed by ^1H, ^{13}C NMR, IR, and elemental analyses.

Table 1 summarizes the photophysical data of compounds **5**–**10**. The UV–vis spectra of all compounds exhibit intense absorption bands between 284 and 386 nm, indicating that electronic transitions are mostly π–π^*, originating from the phenyl and pyridyl groups as previously reported (Fig. 1).[9]

All compounds yield blue emission in solution at room temperature. The observed broad emission bands are predominantly attributed to fluorescence as supported by small Stokes shift and their relatively short decay lifetime. The red-shift of the emission energy of these compounds, compared to that of 2,2′-dipyridylamine ($\lambda_{max}=343$ nm in solution) or 7-azaindole ($\lambda_{max}=357$ nm in solution), is due to the conjugation of the 2,2′-dipyridylamino unit or the 7-azaindolyl unit with the phenylene unit and the rigid-rod unit containing carbon–carbon triple bonds and the phenyl or biphenyl unit. Similar red-shift of emission energy in related 2,2′-dipyridylamine derivatives has also been recently reported by our group.[10]

Photoluminescent efficiencies of **5**–**10** in solution were determined by using 9,10-diphenylanthracene as the standard. The data shown in Table 1 indicate that these new molecules are highly efficient emitters. As the degree of conjugation increases from **7** to **10**, the emission energy of these compounds decreases, consistent with $\pi\rightarrow\pi^*$ transitions. Compounds **8**–**10** have the emission maximum in the blue region, which along with their high emission efficiency, makes them potential blue emitters for organic-light-emitting devices. The

Table 1. Photophysical data for selected compounds[a]

Compound	Absorption (λ_{max}, nm)	Emission (λ_{max}, nm)	Decay lifetime[b] (τ, μs)	Quantum[c] yield (Φ_{em})
5	324	361	3.7	0.69
6	332	382	3.6	0.76
7	344	386	4.8	0.79
8	356	405	5.1	0.31
9	360	416	28.5	0.65
10	362	430	29.3	0.73

[a] All data were collected in dichloromethane solution at room temperature (concentration: $[M]=6.7\times10^{-5}$ M).

[b] The decay profiles of all the compounds were composed of two or three exponential functions. However, we present the longest lifetime of each compounds for clarity.

[c] The quantum yields were obtained by comparing to 9,10-diphenylanthracene (0.9) as a reference.

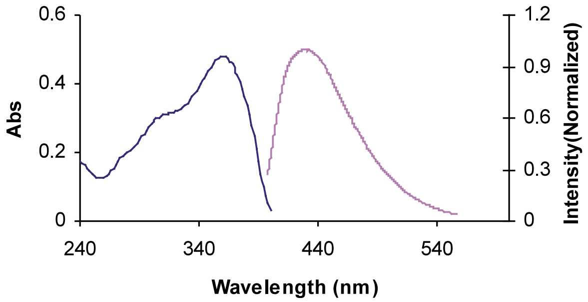


Figure 1. UV–vis absorption and fluorescent emission spectra of **10** in dichloromethane at room temperature.

extended conjugation in compounds **9** and **10** may also be responsible for the enhanced photoluminescent efficiencies for **9** and **10**, compared to that of **8**. Compounds **5**–**10** also display intense phosphorescent emission in the solid state or in solution at low temperature. The details of phosphorescence displayed by these compounds are currently being investigated.

In conclusion, we have achieved the syntheses of a new class of highly efficient blue emitters with rigid-rod structures. From our preliminary investigations of **5**–**10**, some of these new compounds have a high thermal stability and a high glass transition temperature. Further investigation on thermal behavior, electrochemistry, electroluminescent properties and coordination chemistry of these new molecules is in progress.

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