ChemComm

COMMUNICATION

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View Article Online View Journal | View Issue

Cite this: *Chem. Commun.*, 2013, **49**, 6206

Received 16th April 2013, Accepted 22nd May 2013

DOI: 10.1039/c3cc42792g

www.rsc.org/chemcomm

Intramolecular [2+2+2] cycloaddition of bis(propargylphenyl)carbodiimides: synthesis of L-shaped π-extended compounds with pyrrolo[1,2-a][1,8]naphthyridine corner units†

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L-shaped π -extended penta-, hexa-, and heptacycles with a pyrrolo-[1,2-a][1,8]naphthyridine junction were prepared from *N*,*N*'-bis-[2-(2-alkyn-1-yl)phenyl]carbodiimides or their naphthyl analogs *via* Rh(ı)-catalyzed intramolecular [2+2+2] cycloaddition and dehydrogenative aromatization. These L-shaped compounds emit sky-blue, yellow-green, or golden-orange fluorescence, with high quantum yields.

Transition-metal-catalyzed cycloadditions are powerful methods for the synthesis of structurally complex and diverse carbocycles and heterocycles.^{1–3} In particular, the [2+2+2] cycloaddition has become an established tool for construction of a broad variety of polycyclic aromatics and hetero-aromatics such as benzenes, pyridines, and related systems.³ However, the majority of these [2+2+2] cycloaddition reactions involve the use of (1) unsaturated carbon components such as alkenes, alkynes, enynes, dienynes, and endiynes, and (2) a limited number of unsaturated heterocomponents such as carbonyls, imines, nitriles, isocyanates, and isothiocyanates.^{3,4} Furthermore, very few examples^{5,6} of utilizing a fully intramolecular mode of the [2+2+2] cycloaddition with hetero-components have been reported despite that three rings can be constructed in a single reaction.⁴

Herein, we report the unprecedented, fully intramolecular [2+2+2] cycloadditions of bis(propargylphenyl)carbodiimides, and that the aromatized cycloaddition products, L-shaped π -extended penta-, hexa-, and heptacycles with pyrrolo[1,2-a][1,8]-naphthyridine corner units, show unique and interesting photonic and electronic properties, such as high fluorescence quantum yield in polar solvents, and spatially separated HOMOs and LUMOs.

[†] Electronic supplementary information (ESI) available: Experimental details, characterization data, DFT calculations, and complete listing for ref. 11. CCDC 924311. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc42792g



Scheme 1 Synthesis of L-shaped (a) pentacycles 4, (b) hexacycles 5, 6, and (c) heptacycles 7.

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We also note that L-shaped pentacyclic compounds with a 6–6–6–5–6 ring system have been investigated to a small extent,⁷ and no studies of hexacyclic and heptacyclic L-shaped compounds have been reported.

Scheme 1 shows the synthesis of L-shaped pentacycles 4, hexacycles 5, 6, and heptacycles 7. Carbodiimide 1a (R = Me) was converted into 4a in an isolated yield of 90% by means of the intramolecular [2+2+2] cycloaddition using Wilkinson's catalyst, followed by dehydrogenation with MnO₂ (Scheme 1). Similarly, 4b (R = pent), 5a,b, 6a,b, and 7a,b were synthesized from 1b, 2a,b, and 3a,b in 93%, 52%, 86%, 65%, and 79% yields, respectively (see ESI† for the details). In the [2+2+2] cycloaddition of unsymmetrical naphthyl phenyl carbodiimides 2, two regioisomers of hexacycles 5a,b and 6a,b were obtained as a mixture in 52% yield (51:49) for a (R = Me) and 86% yield (53:37) for b (R = pent). The isomers 5a,b and 6a,b were then separated by fractional recrystallization. The structure of 5a was determined by the X-ray analysis (Fig. S1, ESI†).⁸



Fig. 1 Frontier MOs and energy levels of 4a, 5a, 6a, and 7a. The vacuum level: 0 eV.

The L-shaped molecules can be regarded as π -extended indolizines (pyrrolo[1,2-a]pyridine).9 Density functional theory (DFT) calculations revealed that an extended HOMO resides on the electron-rich pyrrole ring, whereas the LUMO mostly resides on the electron-deficient pyridine ring.9b,10 We envisioned that if such an electronic feature was preserved in the L-shaped molecules, their HOMOs and LUMOs would be spatially separated, which would enable us to set the HOMO and LUMO energy levels independently. To determine the electronic structures of the L-shaped compounds, DFT computations at the B3LYP/6-31G(d,p) level were carried out for 4a, 5a, 6a, and 7a using the Gaussian 03 program package (Fig. 1).¹¹ As expected, the HOMOs are primarily on the pyrrole-containing sides, while the LUMOs are on the pyridine-containing sides; therefore, their HOMO and LUMO energy levels are significantly influenced by the side on which their lobes reside. The HOMO levels of molecules with the same pyrrole-containing side were comparable (the 4a (-4.96 eV) and 5a (-5.00 eV) pair compared with the 6a (-4.76 eV) and 7a (-4.82 eV) pair), as are the LUMO levels of molecules with the same pyridine-containing side (for example, the 4a (-1.81 eV) and 5a (-1.91 eV) pair compared with the 6a (-2.13 eV) and 7a (-2.18 eV) pair).

Fig. 2 shows the UV-vis absorption, fluorescence spectra, and photographs under irradiation with UV light of 4a, 5a, 6a, and 7a in dichloromethane, and the spectral and the electronic data are summarized in Table 1. Prominent features observed are as follows. (i) Absorption and emission bands were red-shifted with an increase in the π -conjugation length from 4 to 7, indicating effective conjugation over the skeleton. The time-dependent (TD)-DFT calculations were in good qualitative agreement with λ_{\max} (abs). The lowest energy absorption bands are assignable to the intramolecular charge-transfer transition from the HOMO to the LUMO with an oscillator strength (f) of 0.29–0.36 (also see ESI⁺); (ii) the compounds showed sky-blue to golden-orange fluorescence with high quantum yields. The fluorescence wavelengths depended on the number of fused rings-4a (sky-blue, $\Phi_{\rm F}$ = 0.83), 5a (yellow-green, $\Phi_{\rm F}$ = 0.76), 6a (yellow-green, $\Phi_{\rm F}$ = 0.76), and 7a (golden-orange, $\Phi_{\rm F}$ = 0.67); (iii) even though these compounds comprise a donor (pyrrole ring)-acceptor



Fig. 2 (a) UV-vis spectra, (b) fluorescence spectra (excited at $\lambda_{max}(abs)$), and (c) photographs under irradiation with UV light ($\lambda = 365$ nm) in CH₂Cl₂ of **4a**, **5a**, **6a**, and **7a** (from left to right).

					Calculatior	1						
Compound	$\lambda_{\max}(abs)^{a} (nm) [\epsilon (10^{4} \text{ cm}^{-1} \text{ M}^{-1})]$	$\lambda_{\max}(\mathrm{em})^{a,b}$ (nm)	${\varPhi_{\rm F}}^{a,b}$	τ_{s}^{a} (ns)	$\lambda_{\max}(abs)$	f^c	$E_{\mathrm{p,a}}^{\mathrm{ox}\ d,e,f}\left(\mathbf{V}\right)$	$E_{1/2}^{\operatorname{red} a,d}\left(V\right)$				
4a	442 (1.4), 421 (1.9), 403 (1.4, sh)	474, 508	0.83	5.44	433	0.31	0.40	-2.40				
5a	479 (1.6), 451 (2.1), 429 (2.0)	523, 544	0.76	6.09	479	0.36	0.52	-2.10				
6a	483 (1.6), 455 (2.3), 432 (1.6)	512, 544	0.76	5.95	482	0.29	0.32	-2.30				
7a	517 (1.6), 485 (2.1), 434 (2.6)	556, 583	0.67	6.34	520	0.33	0.32	-2.04				
^{<i>a</i>} In CH ₂ Cl ₂ . ^{<i>b</i>} Excitation at λ_{max} (abs). ^{<i>c</i>} Oscillator strength. ^{<i>d</i>} Potential ν s. ferrocenium/ferrocene. ^{<i>e</i>} In THF. ^{<i>f</i>} Irreversible.												

Table 2 Photophysical properties of 4b in various solvents

Solvent	$\lambda_{\rm max}({\rm abs})~({\rm nm})~[e~(10^{-4}~{\rm cm}^{-1}~{\rm M}^{-1})]$	$\lambda_{\max}(\mathrm{em})^a (\mathrm{nm})$	${\Phi_{ m F}}^a$	$\tau_{\rm s}{}^a$ (ns)	Stokes shift (cm ⁻¹)
Methanol	444 (1.1), 422 (1.8), 404 (1.4, sh)	473, 507	0.83	6.90	1380
Dichloromethane	448 (1.4), 425 (1.9), 406 (1.4, sh)	477, 512	0.82	5.78	1360
Hexane	455 (1.5), 428 (2.0), 405 (1.4, sh)	462, 495, 531	0.80	4.26	330
	``````````````````````````````````````				

^{*a*} Excitation at  $\lambda_{\max}(abs)$ .

(pyridine ring) heterojunction, they exhibited weak solvatochromism (0–0) emission band of **4b** at 473 nm in MeOH and at 462 nm in hexane, and their fluorescence was hardly quenched in polar solvents ( $\Phi_{\rm F}$ : 0.83 in MeOH and 0.80 in hexane, Table 2);¹² (iv) cyclic voltammetry studies in dichloromethane and THF (summarized in Table 1) revealed that the first oxidation potentials,  $E_{\rm p,a}^{\rm ox}$ , are affected mainly by the pyrrole-containing sides of the L-shaped molecules (note that  $E_{\rm p,a}^{\rm ox}$  of **5a** is similar to that of **4a**). On the other hand, the first reduction potentials,  $E_{1/2}^{\rm red}$ , greatly depend on the electronic structure of the pyridine-containing sides (note that  $E_{1/2}^{\rm red}$  of **5a** is similar to that of **7a**). These results are consistent with the DFT calculations mentioned above.

Table 1 Photophysical and electrochemical properties of L-shaped compounds

In conclusion, we demonstrated a useful, one-flask synthesis of penta-, hexa-, and heptacyclic L-shaped  $\pi$ -extended compounds with a pyrrolo[1,2-*a*][1,8]naphthyridine junction, based on the rhodium(1)-catalyzed [2+2+2] cycloaddition of *N*,*N'*-bis-[2-(2-alkyn-1-yl)phenyl]carbodiimides or their naphthyl analogs. The L-shaped compounds emit sky-blue to golden-orange fluorescence in high quantum yields, even in polar solvents. Cyclic voltammetry studies and DFT calculations indicate that the HOMO and LUMO energy levels mostly depend on the  $\pi$ -system of the pyrrole- and pyridine-containing sides, respectively.  $\pi$ -Elongation from 4 to 5, and from 4 to 6, demonstrated independent depression of the LUMO and elevation of the HOMO levels, respectively, offering a new electronic tuning method using these L-shaped structures.

We thank the Ministry of Education, Culture, Sports, Science, and Technology of Japan for the Grant-in-Aid for Specially Promoted Research (No. 19002008).

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