Synthesis and electronic properties of novel 5,7-diazapentacene derivatives

Andrey V. Lunchev,[a] Samuel A. Morris,[a] Rakesh Ganguly,[b] and Andrew C. Grimsdale[a]†

Abstract: A route to the synthesis of novel 5,7-diazapentacenes and some preliminary studies on their properties is reported. A single crystal X-ray diffraction study of the dihexyl derivative showed it had formed a dimer during the analysis. The materials possess lower lying frontier orbitals than pentacene, and may have potential applications in organic electronic devices. This synthetic method may be applicable to the synthesis of other azaacenes.

Introduction

Acenes [1] are one of the most heavily investigated classes of organic semiconductors, due to the exceptionally high (>10 cm^2/Vs) charge carrier mobilities measured in single crystals of these materials such as pentacene (**1**) and rubrene (**2**).[2] Charge carrier mobilities above 1 cm^2/Vs have also been measured in field effect transistors (FETs) using thin films of solution processable pentacene derivatives such as TIPS-pentacene (**3**).[3] While these acenes are p-type materials, the incorporation of nitrogen atoms into the aromatic core of acenes such as pentacene increases their electron affinity and lowers the frontier molecular orbital energies, making them better electron acceptors and transporters. As a result, tetraazapentacene analogues of TIPS-pentacenes such as **4** are n-type semiconductors.[4] Thus, pyrazinacenes such as **4** which contain pyrazine rings have become widely studied materials due to their potential application as n-type semiconductors in OFETs and other organic electronic devices,[1] and there exist well developed procedures for their synthesis.[5-7]

However, some nitrogen doped acenes, which could be important for elucidating structure-property relations such as 5,7-diazapentacene (quinolino[3,2-b]acridine) (**5**), have never been synthesized, and, thus, studied. The only reported attempt to synthesize **5** was unsuccessful.[8] In our previous report, we tried to obtain the 12,14-dihexyl derivative **6a** by means of a Friedländer reaction followed by dehydrogenation of the octahydroacene **7**.[9] However, all attempts to dehydrogenate **7** or the dibenzotetrahydroderivative **8** were unsuccessful. We were able to synthesize a 5,7-diazapentacene derivative **9** bearing additional benzene rings by means of a Friedländer reaction followed by oxidation. We now report a synthesis of 5,7-diazapentacenes bearing hexyl (**6a**) and phenyl (**6b**) substituents by a reaction between aryldiaminodiketones and a phenyliodonium salt.

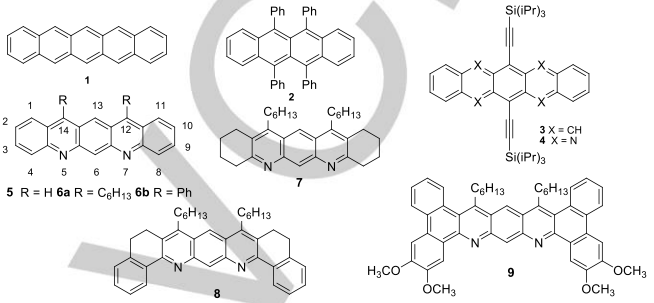


Figure 1. Structures of acenes and azaacenes, their precursors and derivatives.

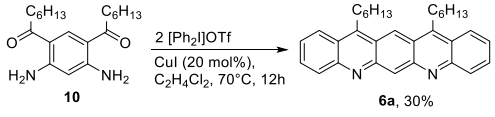
Results and Discussion

Synthesis of 5,7-diazapentacene derivatives

We found that the diaminodiketone **10**, whose synthesis was previously reported by us,[9] reacts with diphenyliodonium triflate[10] in the presence of catalytic amounts of copper (I) iodide in 1,2-dichloroethane (DCE) at 70 °C, to give the 5,7-diazapentacene **6a** in 30% yield. (**Scheme 1**).

The derivative **6b** bearing phenyl groups was synthesized employing the strategy shown in **Scheme 2**. First, 1,5-dimethyl-2,4-dinitrobenzene **11** was obtained by means of nitration. Then **11** was oxidized to the diacid **12** using CrO_3 [11] followed by Friedel-Crafts reaction between the acid chloride and benzene in 1,1,2,2-tetrachloroethylene (TCE) [12] to give **13** in 61% yield. The reduction of **13** by hydrogen at atmospheric pressure in presence of Pd/C gave the desired diaminodiketone **14** in 86% yield. The reaction of **14** with two equivalents of diphenyliodonium triflate leads to the 5,7-diazapentacene **6b** in 55% yield.

The structures of the products **6a,b** were determined by means of ^1H and ^{13}C NMR, and High Resolution Mass Spectrometry (HRMS).



Scheme 1. Synthesis of 5,7-diazapentacene **6a**.

[a] *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798*
[b] *Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore 637371*
† *Author to whom correspondence should be addressed* acgrimsdale@ntu.edu.sg

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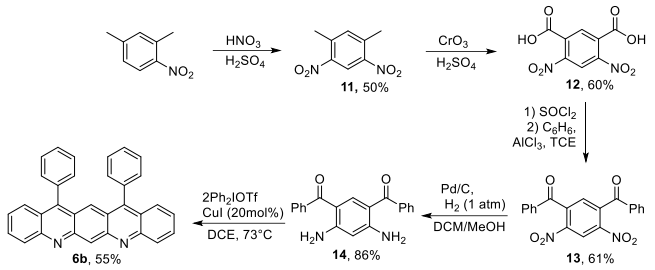

Scheme 2. Synthesis of **6b**.

The Single Crystal XRD (SCXRD) data obtained from crystals grown from a solution of **6a** in 1,2-dichlorobenzene suggests the formation of a dimer (**Figures 2, 3 & 4**). **Figure 2** (top) shows a truncated single dimer molecule of compound **6a** where the C_6H_{13} tails attached to the opposite ring carbon from each nitrogen have been removed for clarity. Hydrogen bonds can be observed as dashed lines; it is these favorable hydrogen bonds which we believe encourage the nitrogen atoms to remain on the same face during dimerization. SCXRD shows the dimer of compound **6a** stacks parallel to the *b*-axis (**Figures 2 & 3**) with all nitrogen atoms on the same side of the molecule. The four nitrogen atoms hydrogen bond with two symmetry-equivalent waters of crystallization, which in turn hydrogen bond to a second water of crystallization. This is unlike our previously reported dimer of tetrahydro-5,7-diazapentacene derivative **8**,[9] (**Figure 2** bottom), which does not crystallize with any water in the structure, and in which the nitrogen atoms in the two units are on opposite sides of the molecule. This indicates that with water in the crystal, the favorable formation of hydrogen bonds encourages the pyridine groups to align in the same direction. By contrast in the dimer of **8** they align in opposite directions, presumably to cancel out the dipoles within the pyridine rings.

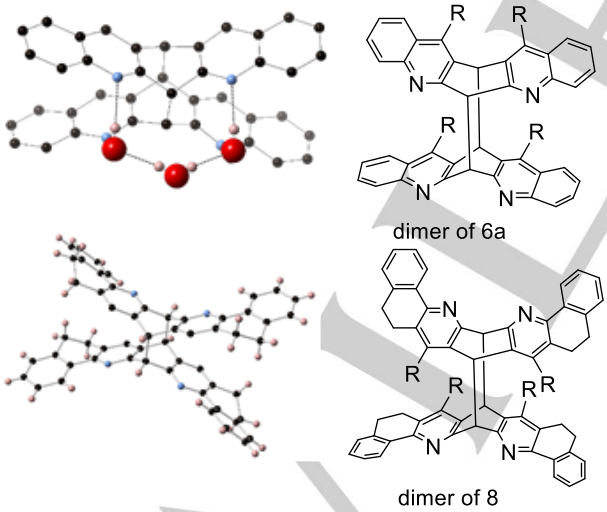

Figure 2. (top) A truncated single dimer molecule of compound 6a. Carbon, oxygen, nitrogen and hydrogen are shown as black, red, blue and pink spheres respectively. Hydrogens attached to the carbon backbone have been removed for clarity. The same colouring scheme is followed throughout the other XRD images. (Bottom) A similarly truncated single dimer molecule of 8 for comparison.[9]

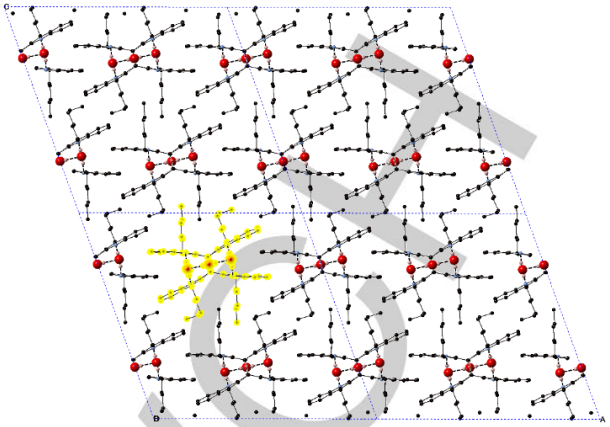

Figure 3. This shows how the x-shaped dimers interconnect in the a-c plane. The long C_6H_{13} chains extend to interact with each other through van de Waals forces. A single unit of the dimer has been highlighted in yellow. The image shows a 2x2x2 supercell of compound **6a** viewed down the b-axis where and the unit cell is shown as blue dashed lines.

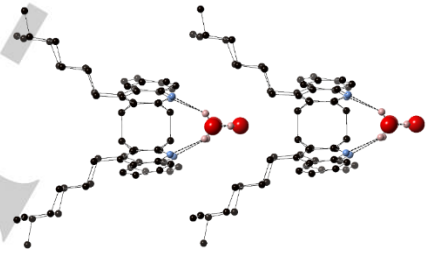

Figure 4: A 'side-on' view of how the dimer stacks parallel to the b-axis. The relationship between the waters of crystallization and the nitrogen from the pyridine rings are also clearly shown.

The dimerization of **6a** prohibits π-π interactions between neighboring molecules, instead, neighboring molecules predominantly interact through van de Waals forces from the long extending C_6H_{13} units as can be seen in **Figure 4**.

The formation of such dimers, sometimes referred to from their shape as 'butterfly dimers', is well known for pentacene derivatives.[13] If, as was originally assumed, it involves a concerted [4+4] cycloaddition it is photochemically allowed but thermally forbidden. However, thermally activated dimerizations of terminally substituted pentacenes have been reported,[13c] and theoretical investigations suggest that it may instead involve a biradical intermediate.[14] The formation of the dimer is favoured by the absence of oxygen as in the presence of oxygen, oxidative decomposition (probably involving an endoperoxide intermediate) is favoured.

The bond lengths between the units in the dimer were 1.620(6) Å for the C2-C2 bond and 1.636(6) Å for the C5-C5 bond. These values are within an acceptable uncertainty of 0.02 Å from each other, and from values of 1.618(3) Å for the dimer of **8** previously reported by us,[9] and 1.604(2) for a pentacene dimer.[13a]

We have not been able to definitively establish whether the dimerization happens during XRD measurements or during the crystal growth. The absence of any signals from the dimer in the NMR spectra or mass spectra of **6a**, and the formation of a dimer

during an XRD experiment for a similar molecule (**8**) reported previously by us [9] suggests that dimerization happens upon the exposure to X-Ray radiation. Supporting this, the crystals supplied for the XRD experiment were purple but the crystal used appeared colourless after the XRD experiment. UV irradiation of **6a** either in solution or the solid state did not result in formation of the dimer, but appeared from NMR and mass spectral data to mainly produce partial decomposition of the molecule, though a weak signal corresponding to the mass of the dimer was observed in the mass spectrum. We did not succeed in growing single crystals of **6b** suitable for SCXRD analysis due to its low solubility in organic solvents. It was noted that samples of **6b** left in the light for several days started to become colorless, which NMR and mass spectral analysis suggested was largely the result of partial decomposition, with only a weak signal corresponding to a dimer being seen in the mass spectrum. This suggests **6b** is less stable than **6a**. A sample of **6b** in CD_2Cl_2 – CF_3COOD showed no sign of decomposition after several days exposure to light, suggesting acid may stabilize these molecules. Further experimental and theoretical investigation will be required to fully explain the formation of the dimer of **6a**. If a way can be found to produce significant quantities of the dimer it would be interesting to study its binding with metal ions. Further exploration of the ability of water molecules to direct the direction of stacking is another area of future research which might produce interesting results.

Electronic properties

The optical absorption spectra of **6a** and **6b** are shown in **Figure 5**. Both the spectra exhibit very similar pattern, with a slight red shift of the signals for **6b**. The values of λ_{max} and λ_{onset} are given in **Table 1**. Based on these values, the compounds have a band gap E_g of 1.7 for **6a**, and 2.0 for **6b**. Unlike **7**, **6a** and **6b** demonstrate no fluorescence and are black colored solids. Samples have been supplied to collaborators for more detailed investigations of their optical properties.

Both **6a** and **6b** demonstrate two irreversible reductive and oxidative peaks in CV using $FeCp_2/FeCp_2^+$ as internal standard (**Figure 6**) from which their HOMO and LUMO energy levels were calculated using the following equations:[15]

$$E\ (HOMO) = -(E_{ox}^{onset}(vs.\ FeCp_2/FeCp_2^+) + 5.10)$$
$$E\ (LUMO) = -(E_{red}^{onset}(vs.\ FeCp_2/FeCp_2^+) + 5.10)$$

They exhibit very close values of oxidation potentials of 0.4 and 0.6 V corresponding to HOMO energies of -5.2 and -5.4 eV respectively. The values of reduction potentials are -1.3 V and -1.4 V corresponding to a LUMO energy value of -3.5 eV and -3.6 eV respectively. Thus, based on the results from CV, the compound **6a** has a band gap of 1.7 eV and **6b** of 1.8 eV. For comparison, the reported values for pentacene of -5.00 and -3.20 eV,[16] and -5.40 and -3.40 eV for an inseparable mixture of 1,8- and 1,11-diazapentacenes.[17] Those values were calculated using a value of -4.8 eV for $FeCp_2/FeCp_2^+$ and must be lowered by 0.3 eV to be directly compared with our values.

As can be seen from Table 1, the new azaacenes **6a** and **6b** demonstrate similar values for HOMO and LUMO to the mixture of 1,8- and 1,11-diazapentacenes. These results confirm that the incorporation of nitrogen atoms into the pentacene aromatic system lowers the energy levels of the frontier orbitals.

These results suggest that 5,7-diazapentacene derivatives might have potential applications in n-type or ambipolar transistors as has been found for 1,8- and 1,11-diazapentacenes.[17] Samples of **6a** and **6b** have been supplied to collaborators to investigate more fully their electrical properties.

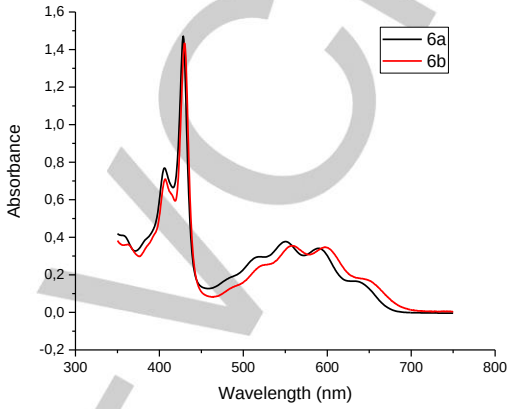

Figure 5. UV-Vis absorption spectra of **6a** (black) and **6b** (red)

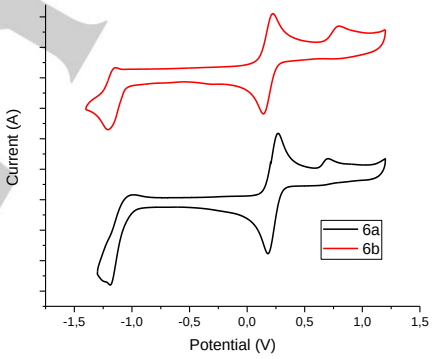

Figure 6. CV plots for **6a** (black) and **6b** (red) scanned at 50 mV/s.

Table 1. Optical, electrochemical, and electronic properties of **6a,b**.

	6a	**6b**
λ_{max} (nm)	429, 551	430, 558
λ_{onset} (nm)	674	687
E_{onset}^{red} vs. Fc/Fc^+ (V)	-1.3	-1.4
E_{onset}^{ox} vs. Fc/Fc^+ (V)	0.4	0.6
HOMO level (eV)	-5.2	-5.4
LUMO level (eV)	-3.5	-3.6
E_g [from CV] (eV)	1.7	1.8
E_g [Optical] (eV)	1.7	2.0

Conclusions

A procedure for synthesis of 5,7-diazapentacene derivatives has been established. Such molecules are reported in literature for the first time. Single crystal X-ray diffraction analysis of a crystal of a dihexyl derivative revealed formation of a dimer, apparently during the X-ray diffraction experiment. The measured optical and electrical properties of the new materials suggest that appropriately functionalized 5,7-diazapentacene derivatives may be suitable for applications in organic electronic devices. The synthetic method used may be applicable to synthesis of other azaacenes.

Experimental Section

Reagents were purchased from Sigma-Aldrich and used as received. Diphenyliodonium Trifliorosulfate was synthesized according to a known procedure.[18] Chromatographic purification was performed as flash chromatography with silica gel (40−65 μm) and solvents indicated as eluent with 0.1−0.5 bar pressure. For quantitative flash chromatography, technical grades solvents were utilized. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 μm F254 TLC glass plates. Visualization was accomplished with UV light. Details of SCXRD, UV-Vis and CV experiments, NMR, mass spectra, and SCXRD crystallographic data are provided in the Supporting Information.

1,5-dimethyl-2,4-dinitrobenzene(11) A literature procedure was used.[19] 25 g (22.4 ml, 0.13 mol) of 1,5-dimethyl-2,4-dinitrobenzene were dissolved in 60 ml of 98% H_2SO_4 at 15 °C. Then 12 ml of 70% HNO_3 was added within 1 h at a rate such that the temperature did not exceed 15 °C. The reaction mixture was stirred for 1 h, poured onto the mixture of ice and water, the resulting precipitate was filtered and washed with water. The solid was recrystallized from methanol (100 ml) two times to produce 16.5 g of the product (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (1H, s), 7.38 (1H, s), 2.70 (6H, s). ^{13}C NMR (400 MHz, $CDCl_3$) δ 146.74, 138.99, 137.30, 121.79

4,6-dinitroisophthalic acid (12). Modified literature procedure [2] was used. A solution of 1,5-dimethyl-2,4-dinitrobenzene (15.7 g, 80 mmol) in 120ml of 98% H_2SO_4 was added within 2 h to a mixture of chromium (VI) oxide (40.0 g, 400 mmol) and 140 ml of 98% H_2SO_4 in a rate that the temperature did not increase above 15 °C. The mixture was stirred with cooling until the temperature dropped to 5 °C, then it was stirred for 2 h at room temperature. The mixture was then poured onto ice and extracted with diethyl ether. The organic phase was collected, evaporated, dissolved in water, filtered, washed with dichloromethane (DCM), then extracted with diethyl ether. The drying of the solution over $MgSO_4$ followed by evaporation gives 12.4 g of the product (60% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.75 (1H, s), 8.31 (1H, s). ^{13}C NMR (400 MHz, DMSO-D_6) 163.80, 148.81, 131.80, 130.67, 120.24

(4,6-dinitro-1,3-phenylene)bis(phenylmethanone) (13). Modified literature procedure [20] was used. 12.3 g (48.0 mmol) 0f 4,6-dinitroisophthalic acid were mixed with 43 ml of $SOCl_2$, then heated for reflux until all the solid had dissolved, which took about 4 h. The excess of $SOCl_2$ was distilled off, after that 45 ml of 1,1,2,2-tetrachloroethane and 20 ml of benzene were added, followed by the addition of $AlCl_3$ (27.8 g, 208 mmol) at 0°C within 40 min. The mixture was stirred overnight at room temperature, the poured into the mixture if methanol (100 ml), ice (100 g) and concentrated HCl (10 ml). The resulting mixture was partially evaporated, mixed with 150 ml of water, and then extracted with dichloromethane. The organic fraction was dried over $MgSO_4$ and evaporated. Column chromatography (Hex:EtOAc = 3:2) afforded 11.0 g of the product (61% yield). %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (1H, s), 7.76 (4H, m), 7.66 (2H, m), 7.59 (1H, s), 7.50 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.49, 146.86, 141.15, 134.86, 134.55, 129.62, 129.41, 129.31, 129.20, 124.78, 121.28

(4,6-diamino-1,3-phenylene)bis(phenylmethanone) (14). A mixture of (4,6-dinitro-1,3-phenylene)bis(phenylmethanone) (11.0 g, 29.2mmol), 2.85 g Pd/C (10% of Pd), 230ml of dichloromethane, and 110 ml of methanol was stirred for 72 h under hydrogen (1 atm). The resulting mixture was filtered through a pad of Celite, evaporated, and purified using column chromatography (DCM:EtOAc = 9:1), to afford 8.0 g of the product (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (1H, s), 7.47 (4H, m), 7.37 (2H, m), 7.30 (4H, m), 6.59 (4H, br. s), 5.81 (1H, s). ^{13}C NMR (400 MHz, $CDCl_3$) 197.11, 155.31, 146.46, 139.87, 130.49, 128.43, 127.90, 110.26, 98.45

12,14-dihexylquinolino[3,2-b]acridine (6a). A mixture of 629 mg (1.9 mmol) of 1,1'-(4,6-diamino-1,3-phenylene)bis(heptan-1-one), 1.670 g (3.9 mmol) of diphenyliodonium triflate, 79 mg (0.4 mmol) of copper (I) iodide, and 20 ml of 1,2-dichloroethane was stirred at 70°C for 12 h under nitrogen. The mixture was quenched with 3ml of concentrated aqueous ammonia and 10 ml of water, extracted with DCM. The organic phase was dried over $MgSO_4$, evaporated, then purified using column chromatography (DCM:EtOAc:Et_3N = 1:1:0.1) producing 255 mg (0.6 mmol, 30% yield) of the product as a black powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (1H, s), 9.21 (1H, s), 8.14 (2H, d, J = 9.09 Hz), 8.08 (2H, d, J = 9.09 Hz), 7.67 (2H, m), 7.36 (2H, m), 3.72 (4H, t, J = 8.08 Hz), 1.89 (4H, m), 1.64 (4H, m), 1.47 – 1.34 (8H, m), 0.93 (6H, t, J = 7.07 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.43, 148.06, 146.18, 130.78, 130.67, 128.32, 125.09, 124.58, 123.97, 123.53, 121.41, 31.78, 31.63, 30.23, 28.21, 22.66, 14.05. HRMS (ESI): $[M + H]^+$ calcd for $C_{32}H_{37}N_2$ m/z 449.2951, found m/z 449.2955 (correct isotope distribution). UV: λ_{max} 429 nm, ε_{max} 7600 L mol^{-1} cm^{-1}.

12,14-diphenylquinolino[3,2-b]acridine (6b). A mixture of 500 mg (1.6 mmol) of (4,6-diamino-1,3-phenylene)bis(phenylmethanone), 1430 mg (3.3 mmol) of diphenyliodonium triflate, 60 mg (0.4 mmol) of copper (I) iodide, and 15 ml of 1,2-dichloroethane was stirred at 70 °C for 12 h under nitrogen. The mixture was cooled down to room temperature, then 10 ml of THF and 2ml of trimethylamine were added. The mixture was filtered, and the black precipitate was washed with THF, then dried in vacuo. Obtained 376 mg (0.9 mmol, 55% yield) of the product as a black powder. ^{1}H NMR (400 MHz, CD_2Cl_2 + CF_3COOD) δ 9.97 (1H, s), 9.10 (1H, br. s), 8.49 (2H, d, J = 3.03 Hz), 8.21 (2H, d, J = 8.84 Hz), 7.89 (2H, m), 7.78 (2H, m), 7.69 (4H, m), 7.53 (4H, m). ^{13}C NMR (400 MHz, CD_2Cl_2 + CF_3COOD) δ 144.99, 143.62, 138.29, 131.86, 131.28, 130.57, 130.51, 129.18, 128.90, 119.76, 119.10, 116.26, 113.41, 110.57, 108.49. HRMS (ESI): $[M + H]^+$ calcd for $C_{32}H_{20}N_2$ m/z 433.1699, found m/z 433.1695 (correct isotope distribution). UV: λ_{max} 430 nm, ε_{max} 7200 L mol^{-1} cm^{-1}.**s**

Acknowledgements

We gratefully acknowledge funding for this research from the Singapore Ministry of Education through the Academic Research Fund Tier1 (grant RG117/15) and Tier2 (grant MOE2013-T2-2-002). We thank Madame Wong Lai Kwai at Chemistry Department, National University of Singapore for performing the high resolution mass spectra.

Keywords: arenes • synthetic methods • X-ray diffraction • dimerization • cyclic voltammetry

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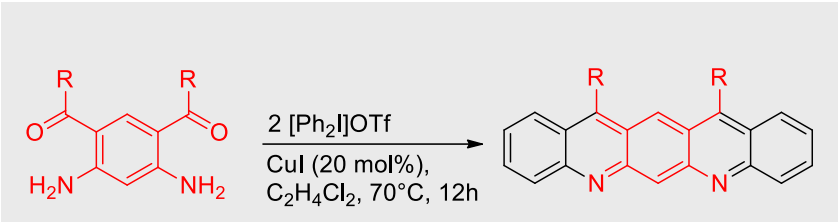

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