

ORIGINAL RESEARCH

Synthesis of Phenanthroline-Based Polyphenylenes *via* a Diels-Alder cycloaddition Reaction

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Abstract

Conjugated polyarenes have been the focus of considerable interest due to their potential for serving as materials for electroluminescence devices, since they possess high fluorescence efficiency and are technically processable. A novel Family of phenanthroline-based compounds were synthesised *via* a [2+4] Diels-Alder cycloaddition reaction between specifically designed cyclopentadienone based synthons that incorporate the already fused phenanthroline moiety 11b-Hydroxy-1,3-diphenyl-1,11b-dihydro-7,8-diaza-cyclopenta[l]phenanthrene-2-one (**1a**) and 11b-Hydroxy-1,3-di(4-*tert*-butylphenyl)-1,11b-dihydro-7,8-diaza-cyclopenta[l]phenanthrene-2-one (**1b**) and various di-substituted acetylenes. These systems have been found to display tuneable fluorescent capabilities, which make them promising material for application in optoelectronics as well showing excellent metal coordination potential.

Keywords: Luminescent, fluorescent, optoelectronic, PAH, HBC, N-HSB, cyclodehydrogenation

Introduction

Energy is one of the most important factors to influence human society in the 21st century.^{1,2} Cost, availability and sustainability of energy have a significant impact on the quality of human standard lives, the development of the global economy, relationship between nations and the stability of the environment. Scientists are now focusing on the development of renewable energies generated from the primary natural resource sunlight and its secondary sources i.e. wind, rain, tides and geothermal heat.^{1,2} Sun has the potential to make the largest energy contribution: only one hour of sunshine (3.8×10^{23} kW) is more than enough to satisfy the highest human

demand for energy for an entire year (1.6×10^{10} kW in 2005).¹ Solar cells, also called photovoltaics, are devices based on solar technology which convert sunlight directly into electricity under the photovoltaic effect.

In organic chemistry, benzene is a natural constituent of crude oil and may also be synthesized from other compounds present in petroleum. By using benzene as a building block, polyphenylene-based materials can be synthesized, extendable in one, two, or three dimensions. The benzene moiety thereby provides a reliable platform for the design of functionality and

demanding structural architectures.^{3,4} As one-dimensional systems, linear conjugated polyphenylenes are considered to play a very important role in the field of organic electronics.³ As two-dimensional compounds, extended planar graphene molecules and their derivatives possess some unique properties, such as strong π - π interaction and self-organisable behaviour.³ In the three-dimensional realm, polyphenylene dendrimers provide many possibilities to obtain multifunctional materials, such as multi chromophores, which can more efficiently harvest light from the sun.^{3,5,6} Due to the presence of different functionalizations of these materials, e.g. electron-rich and electron-poor moieties or solubilising alkyl chains with different lengths, it is possible to fine-tune the photophysical and electrochemical properties, solubility, and, consequently, the formation of perfectly self-organisable arrangements. All of these aspects are significantly important for the improvement

of device performance. In considering the uniqueness of polyphenylene-based materials, the present article focuses on synthesis and photophysical properties (e.g., thermal stability, good solubility, processability, and interesting electrical and optoelectronic properties.) of phenanthroline-based polyphenylenes when using N-doped benzene as a regular building block.

As part of a long-standing interest in N-containing polyphenylenes both as synthons in the formation of heteroatomic graphenes and as ligands in coordination chemistry.⁷⁻⁹ The nitrogen-containing polycyclic aromatic hydrocarbons (PAHs) are of particular interest because heteroatoms influence the electronic properties of molecules without modifying the overall structure. For example, all-carbon triphenylenes are p-type semiconductors (Figure 1 (a)) while hexaazatriphenylenes are n-type (Figure 1(b)).^{10,11}

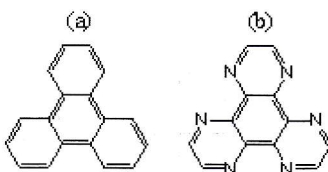


Figure 1: Structures of polyphenylenes (a) all-carbon triphenylenes (p-type) and (b) hexaazatriphenylenes (n-type).

These modified structures are very useful in the development of organised metal-complex systems with variable optical and electrochemical properties. It has been shown that 1,10-phenanthroline (phen),¹² bipyridine

(bpy),^{7,13} and 1,4-diazine derivatives such as dipyrdo[*f,h*]quinoxaline (dpq)¹⁴ (Figure 2) form complexes that are effective luminescent compounds in both solid state (77K) and solution (293K).

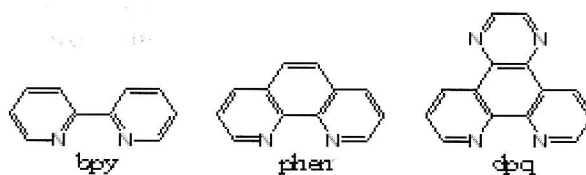


Figure 2: Bipyridine (bpy), 1,10-phenanthroline (phen) and dipyrdo[*f,h*]quinoxaline (dpq).

Draper and Müllen among others have modified the periphery of the hexabenzocoronene (HBC) by introducing heteroatoms, for example nitrogen (a) and sulphur (b) (Figure 3).^{9,15,16} The systematic replacement of carbon atoms with electronegative nitrogen atoms enhances the electronic properties of the system

because of the higher electron density.⁹ However, the inclusion of nitrogen donor atoms renders the HBC-type core overall electron-accepting. This confers on the new nitrogen-heterosuperbenzenes (N-HSBs) (Figure 3 (a)) the dual advantage of ligand functionality^{7,8,13} and increased solubility when compared to their all-carbon analogues.⁹

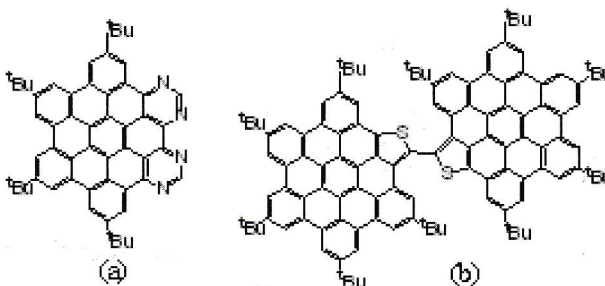


Figure 3: PAHs: (a) N-doped periphery (N-HSB) and (b) S-doped periphery (S-HSB).

Materials and Methods

These extended aromatic platforms are synthesised *via* the [2+4] Diels-Alder cycloaddition reaction of cyclopentadienones with suitable di-substituted dipyrindyl acetylenes acting as a source of N-heteroatoms. The key step in their synthesis is the cyclodehydrogenation of the nitrogen containing polyphenylene formed on cycloaddition reaction. This step however can be systematically challenging as the inclusion of nitrogen atoms in the periphery renders the reaction less efficient, and can result in a mixture of fully-fused and partially-fused products.¹⁷ In an effort to circumvent this difficulty, a new approach was adopted. The design of a novel cyclopentadienone synthon that incorporates an already fused phenanthroline moiety. It was reasonable to expect that the efficiency of the cyclodehydrogenation step would improve with the reduction of the number of nitrogen atoms 4 to 2. Such reduction was possible in this case because there was no possibility of

forming structural isomers as the rings bearing the nitrogen atoms are already fused into position.

Results and Discussion

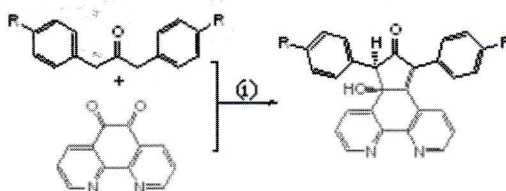
Extended N-doped polyphenylenes have been synthesised using 1,10-phenanthroline, however there are only a few reported in literature (e.g. dipyrido[*f,h*]quinoxaline (dpq) and 6,7-dicyanodipyrido[2,2-*d*;2',3'-*f*]quinoxaline (dicnq)).¹⁸ Therefore, there is considerable scope to develop the synthetic protocol to produce new phenanthroline-based platforms as shown in Scheme 2.¹⁷ All the novel compounds 1 to 7 that are given in Scheme 2 were characterised by NMR, Mass, and IR spectroscopy and elemental analysis.

Synthesis of Cyclopentadienone

Tetraarylcyclopentadienones are accessed *via* a two-fold Knoevenagel condensation reaction between 1,3-diarylacetonand a

suitable 1,2-diketone.¹⁹ In order to create a cyclopentadienone with a pre-fused phenanthroline moiety, 1,10-phenanthroline-5,6-dione (1.32 g, 6.28

mmol) and 1,3-diphenylacet-2-one (2.0 g, 9.5 mmol) were stirred with KOH (65 mg, 1.16 mmol) in EtOH (12 mL) (Scheme 1). The product was isolated by recrystallizing with hot ethanol.¹⁷



Scheme 1: Reaction of 1,10-phenanthroline-5,6-dione and 1,3-diphenylacetone. (i) KOH, EtOH. 1a: R=H and 1b: R=CH₃.

Analysis of the resulting products showed that only one molecule of water was lost, yielding 11b-Hydroxy-1,3-diphenyl-1,11b-dihydro-7,8-diazacyclopenta[*l*]phenanthrene-2-one (**1a**) in 87% yield (Scheme 1). Increasing the temperature of the reaction yielded mixture of products and they were difficult to isolate. The phenanthroline-based polyphenylene (**3**) was synthesised *via* Diels-Alder cycloaddition reaction between di(4-*tert*-butylphenyl)acetylene (365.4 mg, 1.26 mmol) and **1a** (510 mg, 1.26 mmol) in 58% yield. The product was precipitated in the reaction mixture and the pure compound was isolated by recrystallizing with dichloromethane/methanol solvent mixture. The success in this reaction illustrated the value of **1a** as a synthetic platform on which to build a novel family of polyaryl ligands incorporating a phenanthroline moiety. To extend the range of ligands synthesised and aid solubility in the final products a second precursor was designed, incorporating tertiary butyl groups on the peripheral phenyl rings in the same way using 1,3-di(4-*tert*-butylphenyl)acetone to afford 11b-Hydroxy-1,3-(4-*tert*-butylphenyl)-1,11b-dihydro-7,8-diazacyclopenta[*l*]phenanthrene-2-one (**1b**) (65% yield) (Scheme 1). Isolation of **1b** was

same as **1a**.

Synthesis of ligands

Despite the need for activation of the hydrocyclopentanone, a wide range of phenanthroline-based ligands (**2-7**) were successfully synthesised *via* a [2+4] Diels-Alder cycloaddition reaction using a variety of substituted acetylenes (Scheme 2). The cycloaddition reaction results in the acetylene functionality being positioned opposite to the phenanthroline moiety, thus facilitating communication through the molecules.²⁰ This family of novel compounds exhibit ligand capabilities through the bidentate N,N-coordination offered by the phenanthroline moiety and in some cases a second possible mode of coordination *via* the inclusion of other heteroatoms.

Table 1: Reaction times and % yields of compounds 2-7.

Ligand	Reaction time [min]	Yield %
2	75	40
3	65	58
4	60	42
5	90	39
6	60	55
7	80	36

Table 1 shows the difference in yield when incorporating heteroatoms into the ligand architecture, with a marked increase in yield observed for the reactions that utilise the all carbon acetylenes (**3** and **6**).

Coordination chemistry

By selecting appropriate metal centres, it was possible to synthesise coordination complexes of both square planar and octahedral geometries as expected for ligands (**2** and **4**). Both Pt(II) and Pd(II) were chosen to exhibit square planar complexes. Molybdenum tetracarbonyls and Ru(II), Os(II) and Ir(III) polypyridyls were employed to impart octahedral geometry on the resulting heteroleptic metal complexes.^[19] Further, ligand **2** was used to synthesise homoleptic Fe(II), Ru(II)

and Os(II) metal complexes to impart octahedral geometry and the reactivity of the d^8 group as shown in Scheme 3.

Molecular structure determination

1a, **1b**, **2** and [PdCl₂(**2**)] were structurally characterised by single crystal X-ray diffraction and they were obtained from a saturated DCM/EtOH solution. The space groups of **1a**, **1b**, **2** and [PdCl₂(**2**)] are orthorhombic Pbc_a, triclinic P-1, triclinic P-1 and monoclinic C2/c respectively. (Figure 4.)

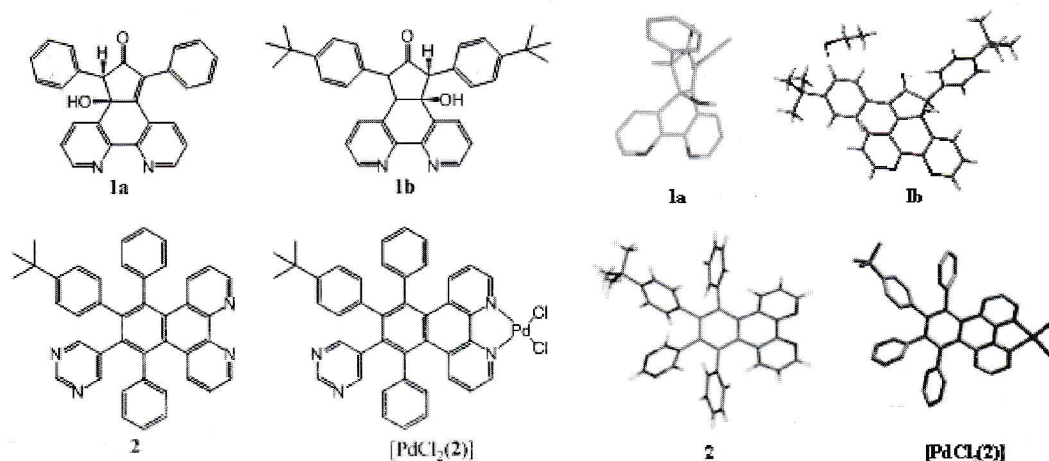
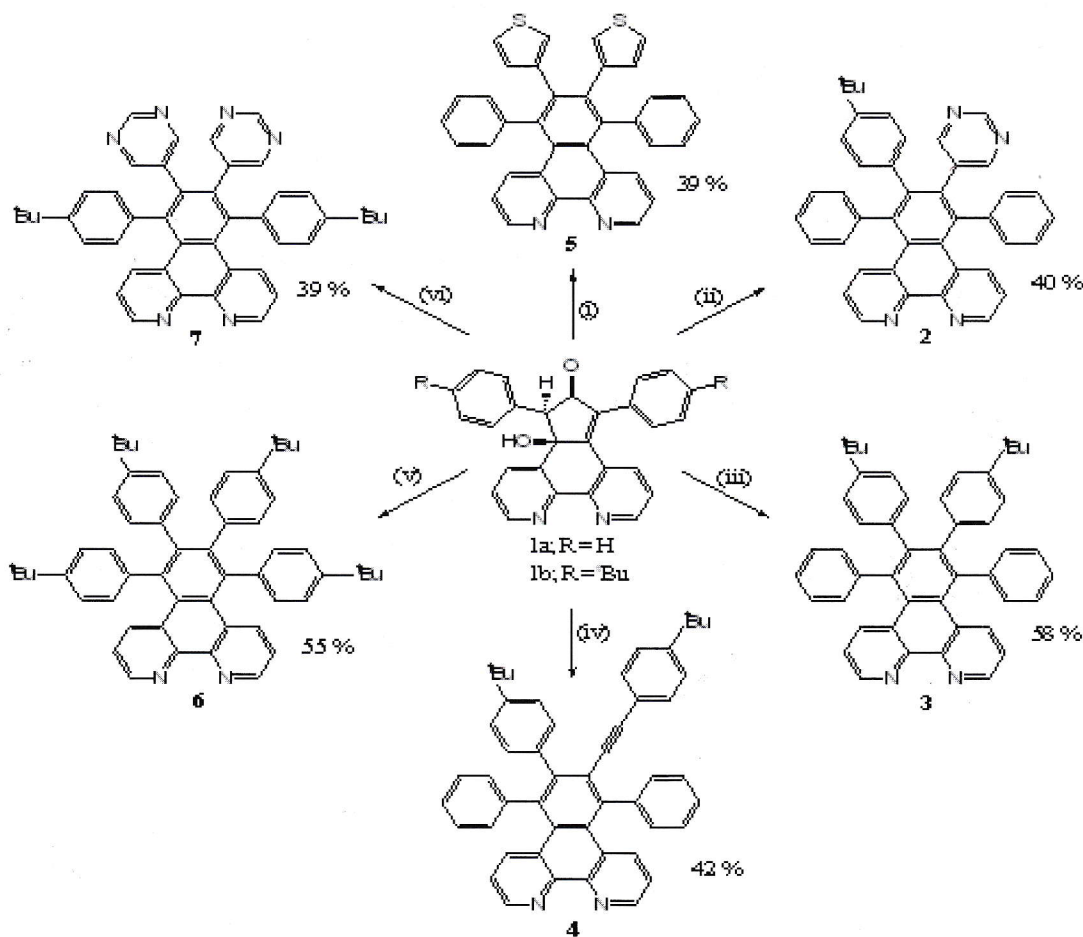


Figure 4: Crystallographic structures of cyclopentadienone with a pre-fused phenanthroline moiety (**1a**) and (**1b**), phenanthroline based ligand (**2**) and [PdCl₂(**2**)].

Photochemistry

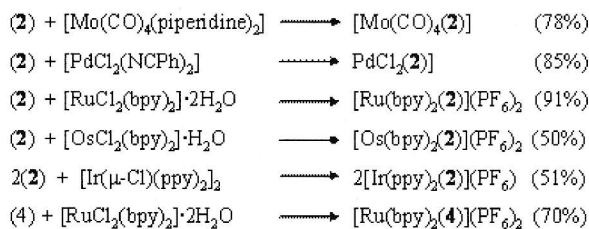
Ogliaruso²² proposed that the structural rigidity and the twist angle between outer rings of polyphenylenes affect their absorption properties. Non-planar biphenyl usually have structureless absorption and emission spectra in solution.²³ On the other hand, planar, rigid molecules with high symmetry such as nitrogen-heterosuperbenzene (N-HSB) show well-resolved vibrational bands with

wide structured absorption and structured fluorescence spectra.¹ The lowest energy transitions of aromatic hydrocarbons are of $\tilde{\pi} \pi^*$ type, and are characterised by their high molar absorption coefficients. When a heteroatom is incorporated in the $\tilde{\pi}$ system, the $\tilde{\pi} \pi^*$ transition may be the lowest energy transition as is observed for pyrimidine.

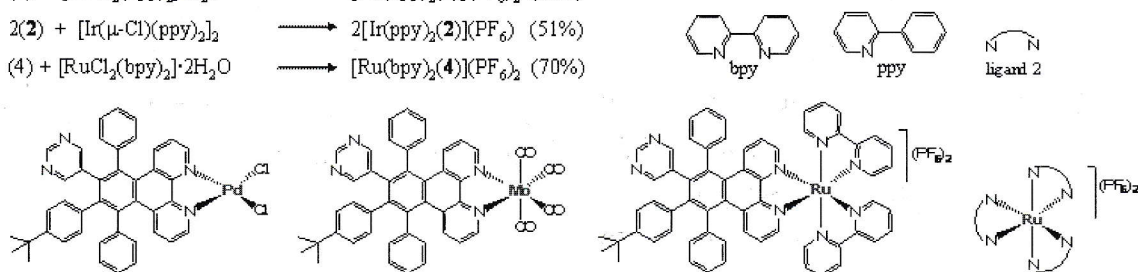
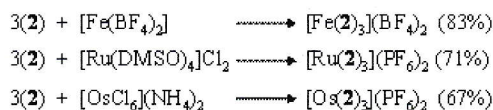


Scheme 2: The versatile and robust nature of the phenbluesynthons evident from the variety of differently functionalised ligands that can be synthesised from [2+4] Diels-Alder cycloaddition reaction between 1a and 1b and various substituted acetylenes. Reaction conditions: 300 °C, Ph₂CO, N₂, (i) di(3-thienyl)ethyne, (ii) 5-(4-*tert*-butylphenyl-ethynyl)pyrimidine, (iii and v) di(4-*tert*-butylphenyl)acetylene, (iv) bis(4-*tert*-butylphenyl)but-1,3-diyne and (vi) di(5-pyrimidyl)acetylene.

Heteroleptic metal complexes of ligand 2 and 4



Homoleptic metal complexes of ligand 2



Scheme 3: Ligand capabilities of compounds 2 and 4 were investigated using *d*⁴ and *d*⁸ metal to synthesise both square planar, hetero- and homoleptic octahedral coordination complexes.¹⁷

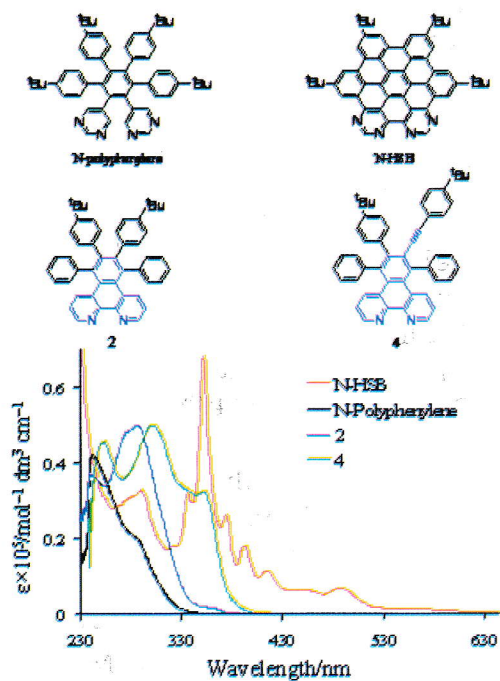


Figure 5: The overlaid absorption spectra of N-doped polyphenylene, N-HSB, phenanthroline-based polyphenylenes 2 and 4 in chloroform.

Figure 5 shows the absorption spectra of 2 and 4. The absorption spectra of 2 and 4 exhibit $\lambda_{\max}^{\text{abs}}$ 288 and 303 nm respectively, whereas N-polyphenylene precursor is hypsochromically shifted to 257 nm due to its reduced planarity. Increased π -conjugation of the system results in gradual red-shift in the absorption maxima (Figure 5). The absorption spectra of fully-cyclised derivative N-HSB displays, well-resolved bands absorbs in the UV-Vis region, compared with the parent N-polyphenylene precursor due the increase in the planarity and the rigidity of the system (Figure 5).

Figure 6 shows the emission spectra of 2 and 4 in chloroform and solid state at room temperature and 77K. These reveal that the emission wavelength has been tuned by the extended π -conjugation compared with N-

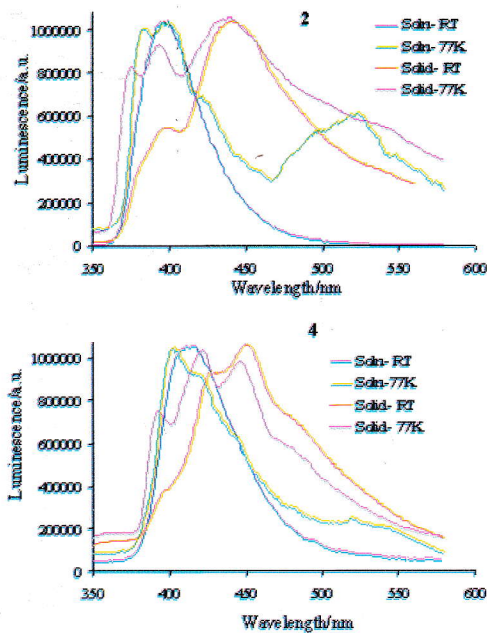


Figure 6: The overlaid emission spectra of 2 and 4 in chloroform and the solid state at room temperature and 77K, λ_{ex} 300 nm.

polyphenylene ($\lambda_{\max}^{\text{em}} = 368$ nm). For example $\lambda_{\max}^{\text{em}}$ of 2 and 4 in chloroform at r.t. is 437 and 452 nm respectively. These observations are due to the reduced energy gap between $\pi \rightarrow \pi^*$ transition (HOMO-LUMO energy gap). In the literature, it has shown that the emission wavelength ($\lambda_{\max}^{\text{em}}$) also can be tuned by varying the number of heteroatoms (nitrogen and oxygen) in the substituents or the periphery of the hexaaryl benzene.¹⁴³ The emission spectra of solid state and in solution at 77K exhibit some vibrational fine structure as expected due to the surrounding rigid matrix. All these ligands (2-7) are luminescent "blue emitters" to the naked eye in the solid state and also in solution under the UV lamp at 365 nm.

Conclusion

In an attempt to synthesise 1,3-diphenyl-7,8-diazacyclopenta[1]phenanthrene-2-one, a more stable hydrated form of this product was isolated. Effectually called "Phenblue" due to its emission in the blue region, this compound act as a synthetic platform from which to prepare polyaromatic phenanthrolines. "Phenblue" undergoes Diel-Alder [2+4] cycloaddition reaction following the *in situ* loss of its hydroxyl group to yield potentially bidentate N,N-coordination ligands for formation of both octahedral and square planar metal complexes. The photophysical attributes of the ligands can be systematically explained by varying the number of heteroatoms incorporated into peripheral atomic substituents and extended π -conjugation with an acetylene unit so as to emit across a wide range of the UV-Visible spectrum.

These novel N-doped phenanthroline-based ligands exhibit promising photophysical properties i.e. thermal stability, good solubility, processability, and interesting electrical and optoelectronic properties. Also they exhibit good ligand stability. Consequently, these N-doped phenanthroline-based polyphenylenes can be used as a regular building block for synthesis of macromolecules by varying the functionality.

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References

1. Goswami, D. Y., Theoretical analysis of a water desalination system using low grade solar heat, *Advances in Solar Energy: An Annual Review of Research and Development*, 2003; 1: 774-80,
2. Delyannis E, . Goswami DY, Belessiotis V. Solar energy and desalination, *Advances in Solar Energy, An Annual Review of Research and Development* 2001; 14: 287-330,
3. Berresheim AJ, Muller M, Mullen K. Polyphenylene Nanostructures, *Chemical Review* 1999; 99: 1747-786,
4. Wiesler UM, Borresheim AJ, Morgenroth F, Lieser G, Mullen K. Divergent synthesis of polyphenylene dendrimers: The Role of Core and Branching Reagent upon Size and Shape, *Macromolecules* 2001; 34: 187-99.
5. Howe L, Zhang JZ. Ultrafast studies of excited-state dynamics of phthalocyanine and zinc phthalocyanine tetrasulfonate in solution, *Journal of Physical Chemistry A* 1997; 101: 3207- 213,
6. Fernandez DA, Awruch J, Dicelio LK, Kubat P, Mosinger J *et al.* Photochemical consequences of porphyrin and phthalocyanine aggregation on nucleoprotein histone, *Journal of Photochemistry and Photobiology A: Chemistry*, 1998; 119: 47-52.
7. Gregg DJ, Bothe E, Höfer P, Passaniti P, Draper SM. Extending the nitro-heterosuperbenzene family: The spectroscopic, redox and photophysical properties of "Half-Cyclized" N-1/2HSB and its Ru(II)

- complex. *Inorganic Chemistry* 2005; 44: 5654,
8. Gregg DJ, Fitchett CM, Draper SM, Intermolecular interactions of extended aromatic ligands: the synchrotron molecular structures of $[\text{Ru}(\text{bpy})_2(\text{N-HSB})] \cdot 2\text{PF}_6$ and $[\text{Ru}(\text{bpy})_2(\text{N-1/2HSB})] \cdot 2\text{PF}_6$, *Chemical Communications*, 3090, 2006.
 9. Draper SM, Gregg DJ, Madathil R, Heterosuperbenzenes: A new family of nitrogen-functionalized, graphitic molecules. *Journal of the American Chemical Society* 2002; 124: 3486-7.
 10. Adam D, Schuhmacher P, Simmerer J, Haeussling L, Siemensmeyer K *et-al.* Fast photoconduction in the highly ordered columnar phase of a discotic liquid crystals. *Nature* 1994; 371: 141-43.
 11. Ishi-I T, Yaguma K, Kuwahara R, Taguri Y, Mataka S, Self-assembling of n-type semiconductor tri(phenanthrolino)hexaazatriphenylenes with a large aromatic core, *Organic Letters* 2006; 8: 585.
 12. Balashev KP, Puzyk MV, Kotlyar VS, Kulikova M, Photophysics, photochemistry and electrochemistry of mixed-ligand platinum (II) complexes with 2-phenylpyridine and 2-(2'-thienyl) pyridine as cyclometalating ligands *Coordination Chemistry Review* 1997; 159: 109-120.
 13. Draper SM, Gregg DJ, Schofield ER, Vos JG., Passaniti P, Complexed nitrogen heterosuperbenzene: The coordinating properties of a remarkable ligand *Journal of the American Chemical Society* 2004; 126: (28), 8694-701.
 14. Balashev KP, Ivanov MA, Taraskina TV, Cherezova EA, Spectroscopic and electrochemical properties of mixed-ligand cycloplatinated complexes based on 2-(2-thienyl)pyridine and 2-phenylpyridine with 1,10-phenanthroline and its 1,4-diazine derivatives *Russian Journal General Chemistry* 2006; 76: 781-90.
 15. Feng X, Wu J, Ai M, Pisula W., Zhi L, *et-al.* Triangle-shaped polycyclic aromatic hydrocarbons. *Angewandte Chemie International Edition* 2007; 119: 3093-96.
 16. Martin C, Perera SD, SM Draper SM. Thiophene containing polyaromatic hydrocarbons. *Advances in Science and Technology* 2008; 54: 120.
 17. Lankage BS. Molecular Materials: N-Doped Graphenes and Their Complexes. Thesis, School of Chemistry, Trinity College Dublin, University of Dublin, 2010.
 18. Ambroise A., Maiya BG. Ruthenium(II) complexes of 6,7-dicyanodipyridoquinoline: Synthesis, Luminescence studies and DNA interaction. *Inorganic Chemistry* 2000; 39: 4264.
 19. Des Abbayes H, Clement JC, Laurent P, Tanguy G, Thilmont N, Scope and mechanism of the phase-transfer carbonylation of organic halides catalyzed by pentacarbonyliron to give

- ketones and carboxylic acids. *Organometallics* 1998, 7, 2293-99.
20. Schelter EJ, Wu R, Scott BL, Thompson JD, Morris DE and Kiplinger JL, Mixed valency in a uranium multimetallic complex. *Angewandte Chemie International Edition*, 47 2008; 2993-96,
21. Borriello C, Centore R and Roviello G, Hydrolysis of Pd(II)-bound acetonitrile: Molecular and crystal structure of the syn isomer of the dinuclear (1,10-phenanthroline)palladium(II) complex bridged with acetamido groups and of its acetonitrile solvate. *Inorganic Chemistry Communication* 2005; 8; 755-58.
22. Ogliaruso MA, Becker EI, Bistetracyclones and bishexaphenylbenzenes, *Journal Organic Chemistry* 1965; 30: 3354-60.
23. Nijegorodov NI, Downey WS. The influence of planarity and rigidity on the absorption and fluorescence parameters and intersystem crossing rate constant in aromatic molecules. *Journal Physical Chemistry* 1994; 98: 5639.