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The synthesis of polyarene-modified 5-phenyl-2,2′-bipyridines *via* the S_N^H methodology and aza-Diels–Alder reaction

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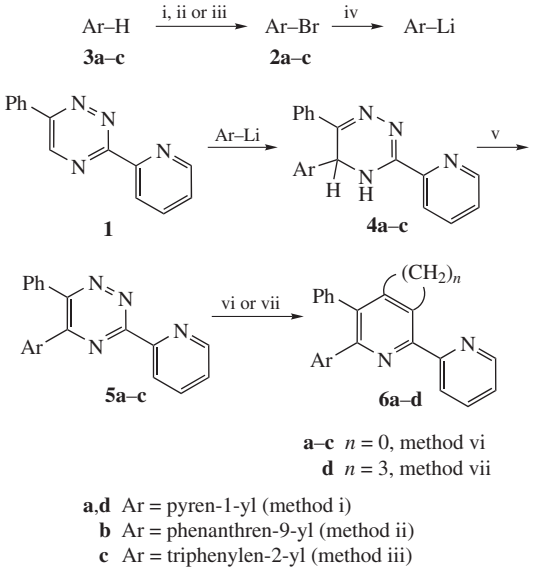
Nucleophilic substitution of hydrogen (S_N^H) in 6-phenyl-3-(2-pyridyl)-1,2,4-triazine under the action of lithium derivatives of polynuclear arenes followed by aza-Diels–Alder reaction with norbornadiene or morpholinocyclopentene gives the novel polyarene-modified photoluminescent 5-phenyl-2,2′-bipyridine ligands.

The polyarene-modified (pyrene, anthracene, naphthalene, *etc.*) 2,2′-bipyridines (bipy) and 2,2′:6′,2″-terpyridines due to their rich photophysical properties,[1] as well as their binding ability to metal cations and DNA, are of wide use as promising components for photochemotherapeutic agents,[2] components for solar cells,[3] chemosensors for various analytes, for instance oxygene[4] or metal cations.[5] In addition, the electrochemical properties of polyaromatic oligopyridines are also of practical interest.[6] The most common synthetic routes to construct the polyarene-modified oligopyridines are the cross-coupling reactions,[7,8] Knoevenagel condensation,[9] a non-direct attachment of polyaromatic chromophores to the oligopyridine core, for instance, *via* the alkyl bridges by the alkylation reactions,[10] and heterocyclization of substituted polyarenes.[11] Finally, 2,2′-bypyridines bearing polyaromatic substituents can be prepared as a mixture of two isomers by the inverse aza-Diels–Alder reaction between 3-(2-pyridyl)-1,2,4-triazines and polyaromatic acetylenes.[12] Most of these methods are often limited by the availability of the starting compounds.

On the other hand, reactions of nucleophilic substitution of hydrogen (S_N^H)[13] are known as a versatile tool for the direct modification of various π-deficient heterocycles, in particular, 1,2,4-triazines,[14] by the residues of electron-rich species. This S_N^H methodology comprising the aza-Diels–Alder reaction was shown to be a promising strategy for the synthesis of 2,2′-bipyridines and 2,2′:6′,2″-terpyridines *via* their 6-Nu-1,2,4-triazine precursors. However, it was limited to activated forms of 1,2,4-triazines, *e.g.* 1,2,4-triazine-4-oxides, and strong nucleophiles, *e.g. in situ* formed cyanide anion, lithium acetylides, lithiumcarboranes.[15] Here we report a versatile synthetic strategy towards novel photoluminescent 5-phenyl-2,2′-bipyridine ligands bearing 6-positioned polyaromatic substituents based on sequence of S_N^H reaction between lithium salts of polyarenes and 6-phenyl-3-(2-pyridyl)-1,2,4-triazine **1** followed by the aza-Diels–Alder reaction of the resulted 5-aryl-1,2,4-triazines (Scheme 1).†

The starting 6-phenyl-3-(2-pyridyl)-1,2,4-triazine **1** was prepared as described.[16] 1,2,4-Triazine moiety is highly π-deficient and is susceptible to form σ-adducts with nucleophiles which can be further aromatized.[17] In this study, aryllithium compounds obtained *in situ* from the corresponding bromoarenes **2** were used as nucleophiles (see Scheme 1). 1-Bromopyrene **2a**[18] and 9-bromophenanthrene **2b**[19] were synthesized by bromination of



a–c $n = 0$, method vi
d $n = 3$, method vii

a,**d** Ar = pyren-1-yl (method i)
b Ar = phenanthren-9-yl (method ii)
c Ar = triphenylen-2-yl (method iii)

Scheme 1 *Reagents and conditions*: i, *N*-bromosuccinimide, CH_2Cl_2, 20 °C, 12 h; ii, Br_2, CCl_4, 77 °C, 2 h; iii, Br_2, CH_2Cl_2, 20 °C, 1 week; iv, Bu^{s}Li, dry THF–dry toluene (1:1), –78 °C → 20 °C, overnight; v, DDQ, CH_2Cl_2, 20 °C, 30 min; vi, 2,5-norbornadiene, *o*-xylene, 143 °C, 18 h; vii, 1-morpholinocyclopentene, *o*-xylene, 143 °C, 10 h.

the parent arenes **3a**,**b**. The procedure for the preparation of 2-bromotriphenylene **2c**[20] was slightly modified: the monobrominated product was obtained only after the prolonged stirring of triphenylene **3c** with bromine in dichloromethane at ambient temperature. Treatment of as-triazine **1** with aryllithium compounds gave the corresponding stable σ-adducts **4** in up to 96% yields. The most practical ratio for **1**:ArLi was 0.8:1, which caused full consumption of triazine **1**, while the excess of ArLi upon work-up was converted back to the arenes **3** easily separable by flash chromatography. The Bu^{s}Li was more effective compared to BuLi which gave admixtures of N-butylated 1,2,4-triazines (ESI-MS data).

The structure of compounds **4** was confirmed by ESI-MS, ^{1}H and ^{13}C NMR and elemental analysis data. ^{1}H NMR spectra of compounds **4** contained signals of protons next to the sp^3-hybridized carbon atom as a one-proton singlet at 6.22–7.00 ppm and the sp^3-hybridized carbon atoms appear in the ^{13}C NMR spectrum as a resonance peaks at 54.9–57.7 ppm, along with the resonances of the NH protons as singlets in the ^{1}H NMR spectrum.

† For procedures and characteristics of compounds, see Online Supplementary Materials.

For the aromatization of σ-adducts **4**, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) is effective.[17(a),21] The products **5** were easily separable by the column chromatography on alumina in up to 91% yields. The structure of **5** was confirmed by ESI-MS, ^{1}H and ^{13}C NMR and elemental analysis data.

1,2,4-Triazine derivatives **5** were converted into pyridines according to the general strategy (see Scheme 1).[22] Their Diels–Alder reaction with 2,5-norbornadiene or 1-morpholinocyclopentene was performed by the prolonged refluxing of the reactants in xylene. Products **6a–c** were purified by column chromatography, poorly soluble compound **6d** was purified by recrystallization. The structures of compounds **6a–d** were confirmed by ESI-MS, ^{1}H and ^{13}C NMR and elemental analysis data.‡ It is worth to mention that due to the pronounced low solubility of pyrene-substituted bipy ligands[1(b)] the use of enamine counterparts seems the good means to enhance the solubility of the target pyrene-substituted oligopyridines and their metal complexes.

In summary, the effective synthetic route towards polyarene-modified 5-phenyl-2,2′-bipyridines is developed. Replacement of pyridine ring in oligopyridine systems by an aryl affords compounds suitable for the preparation of *ortho*-metallated tridentate (C^N^N)-ligands.[23] Being formally anionic, these ligands form stable photoluminescent complexes with d^6 and d^8 transition metals, for instance the cyclometallated complexes of Pt^{II},[12,24] Pd^{II},[25] and Ir^{III}.[26]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.02.018.

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‡ *5-Phenyl-6-(pyren-1-yl)-2,2′-bipyridine* **6a**. Yield 270 mg (0.63 mmol, 79%), mp 214–216 °C. ^{1}H NMR ($CDCl_3$) δ: 7.02 (m, 3H, Ph), 7.09–7.14 (m, 2H, Ph), 7.31 (m, 1H, 5-H_{Py}), 7.75 (ddd, 1H, 4-H_{Py}, ^3J 7.8 and 7.8 Hz, ^4J 1.6 Hz), 7.82 (d, 1H, 3-H_{Pyrene}, ^3J 8.0 Hz), 7.96–8.10 (m, 6H, 3-$H_{Py(center),pyrene}$), 8.12–8.17 (m, 2H, pyrene), 8.19 (d, 4-$H_{Py(center)}$, ^3J 7.8 Hz), 8.49 (dd, 1H, 3-H_{Py}, ^3J 7.8 Hz, ^4J 1.6 Hz), 8.62 (d, 1H, 2-H_{Pyrene}, ^3J 8.0 Hz), 8.74 (dd, 1H, 6-H_{Py}, ^3J 4.8 Hz, ^4J 1.6 Hz). ^{13}C NMR ($CDCl_3$): 119.7, 121.7, 123.8, 124.4, 124.8, 125.0, 125.2, 125.5, 125.9, 127.1, 127.4, 127.5, 127.6, 128.1, 128.5, 129.3, 129.4, 131.0, 131.1, 131.3, 135.8, 136.9, 138.1, 139.2, 139.3, 139.4, 149.2, 154.6, 156.1, 156.8. ESI-MS, *m/z*: 433.17 $[M+H]^+$ (calc., *m/z*: 433.17). Found (%): C, 88.58; H, 4.41; N, 6.27. Calc. for $C_{32}H_{20}N_2$ (%): C, 88.86; H, 4.66; N, 6.48.

For characteristics of compounds **6b–d**, see Online Supplementary Materials.