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Sequential synthesis of rigid multi-bipyridine ligands bearing diethynyl/phenyl solubilizing fragments

Abderrahim Khatyr and Raymond Ziessel *

Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, associé au CNRS, Ecole Chimie, Polymères, Matériaux, 25 rue Becquerel, 67087 Strasbourg, Cédex 02, France

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Abstract

Reliable and practical synthetic routes for the construction of multitopic bipyridine ligands are presented. The first series contains the chelating fragments connected via an ethynyl function and the second series is built from an alternation of ethynyl/phenyl/bipyridine modules. The synthetic protocol is based on sequential Pd-promoted cross-coupling reactions between selected bis-bpy or ethynyl/phenyl/bpy intermediates of increasing size. The ligands bearing functionalized 1,4-diethynyl-2,5-di(dodecyloxy)benzene subunits are soluble in chlorinated solvents. © 2000 Elsevier Science Ltd. All rights reserved.

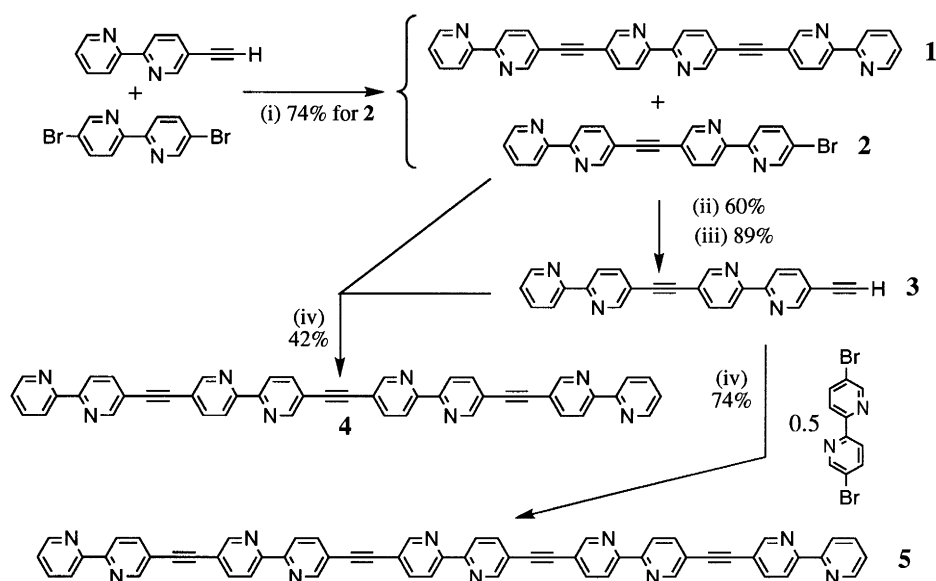
Tremendous innovations in synthetic methodology, together with allied advances in technology, provide new opportunities for the chemist to explore classical problems and to apply the results to newly-emerging disciplines. A good example of this progressive advancement in scientific knowledge concerns the design of materials for use in molecular-scale electronic devices.¹ Following the realization that many simple transition metal complexes with 2,2'-bipyridine (bpy) ligands exhibit outstanding redox and photochemical properties,² strenuous efforts have been made to incorporate such complexes into highly-organized molecular arrays. Subsequent examination by fast laser spectroscopy reveals that such supramolecular systems facilitate rapid energy and/or electron transfer between the individual components. With sophisticated spectroscopic tools it becomes possible to delve deeply into the information transfer mechanism, thereby stimulating rational design of advanced molecular systems. In turn, it leads to interesting synthetic and analytical problems and leads to an exciting iteration of ideas and methodology.³

As regards the construction of linear polynuclear metal complexes having discrete units linked by short, highly-conductive wires, we and others have identified polyynes as being particularly attractive molecular-scale connectors.^{3,4} The interest in such multinuclear complexes is stimulated by the recent structural determinations of photosynthetic light-harvesting complexes and by the realization that these natural antennae effectively delocalize the photon over a large number of spatially remote,

* Corresponding author. Fax: 33 3 88 13 68 95; e-mail: ziessel@chimie.u-strasbg.fr (R. Ziessel)

but chemically identical pigments.⁵ Clear proof that triplet energy migration occurs between terminal metal fragments in artificial systems has not yet been clearly identified despite some hints deduced from transient depolarized measurements.²

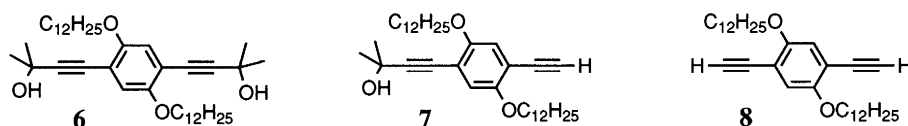
Here we wish to report a synthetic strategy which allows the preparation of stable and quasi-linear multitopic bipyridine ligands which are auspicious for the study of photon shuttling between chromophoric units. One of the most straightforward methods for the synthesis of arylalkynes, conjugated enynes and pyridylalkynes is the palladium-promoted coupling of terminal alkynes with aryl, alkenyl or pyridyl halides which was pioneered by Sonogashira et al.⁶ We have previously found that this reaction is extremely versatile and highly effective when run in the presence of an inordinately wide variety of available oligopyridines.⁷ Here we discovered that mono-functionalization of 5,5'-dibromo-bpy with 5-ethynyl-bpy is effective when the reaction is carried out under specific conditions in the presence of the acetylenic derivative (1 equiv.) as outlined in Scheme 1. The side product assigned as ligand **1** ($\leq 10\%$)⁸ results from a double cross-coupling reaction. The key intermediate **2** was converted to the ethynyl-grafted compound **3** under similar experimental conditions.



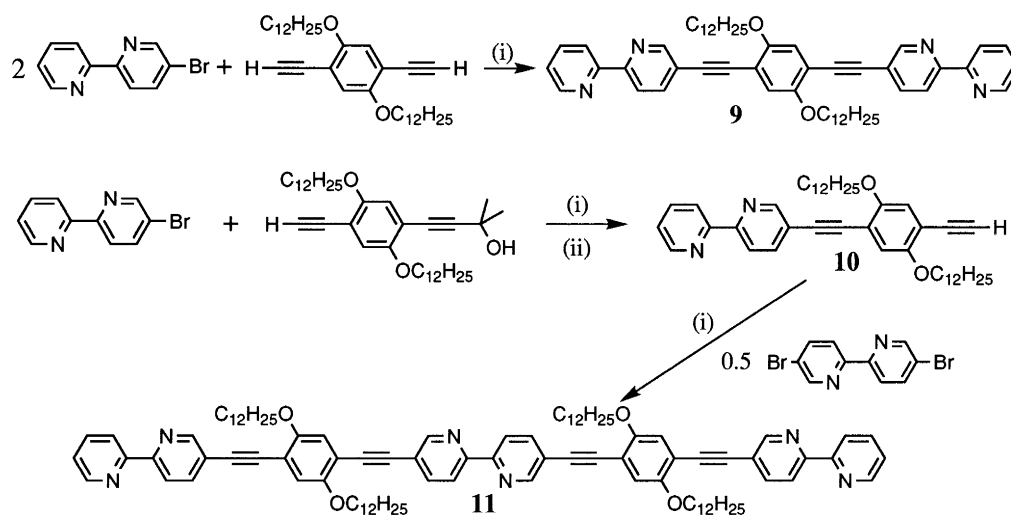
Scheme 1. (i) $[\text{Pd}(\text{PPh}_3)_4]$ (6 mol%), benzene, $^i\text{Pr}_2\text{NH}$, 80°C ; (ii) $\text{TMSC}\equiv\text{CH}$, $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (6 mol%), CuI (10 mol%), THF , $^i\text{Pr}_2\text{NH}$, rt; (iii) K_2CO_3 , CH_3OH , rt; (iv) $[\text{Pd}(\text{PPh}_3)_4]$ (6 mol%), benzene, $^i\text{Pr}_2\text{NH}$, 80°C

Both intermediates **2** and **3** were allowed to react together to give the segmented octapyridine ligand **4** in a modest yield. Furthermore, the reaction of compound **3** with 5,5'-dibromo-bpy (0.5 equiv.) afforded the segmented decapyridine ligand **5**.⁹ Unfortunately, an emerging problem on increasing the size of the system is the drop of solubility as observed for ligands **4** and **5**. Therefore it is desirable to design soluble multicomponent molecules of nanometric dimension without loss of the effectiveness of the electronic conductivity. Solubility and tunability can be achieved by spanning two bpy subunits with substituted diethynylphenyl subunits functionalized with two dodecyloxy moieties.

Here we show that this strategy is successful in generating a family of rigid and multitopic ligands (2 to 5 chelating centers), where the edge-to-edge distance between the two external pyridine rings vary from ~ 21 – 72 Å. The adopted synthetic protocol utilizes the pivotal intermediates **7** and **8**, each of which being readily prepared from synthon **6** by a selective or complete deprotection reaction using NaOH as base.¹⁰



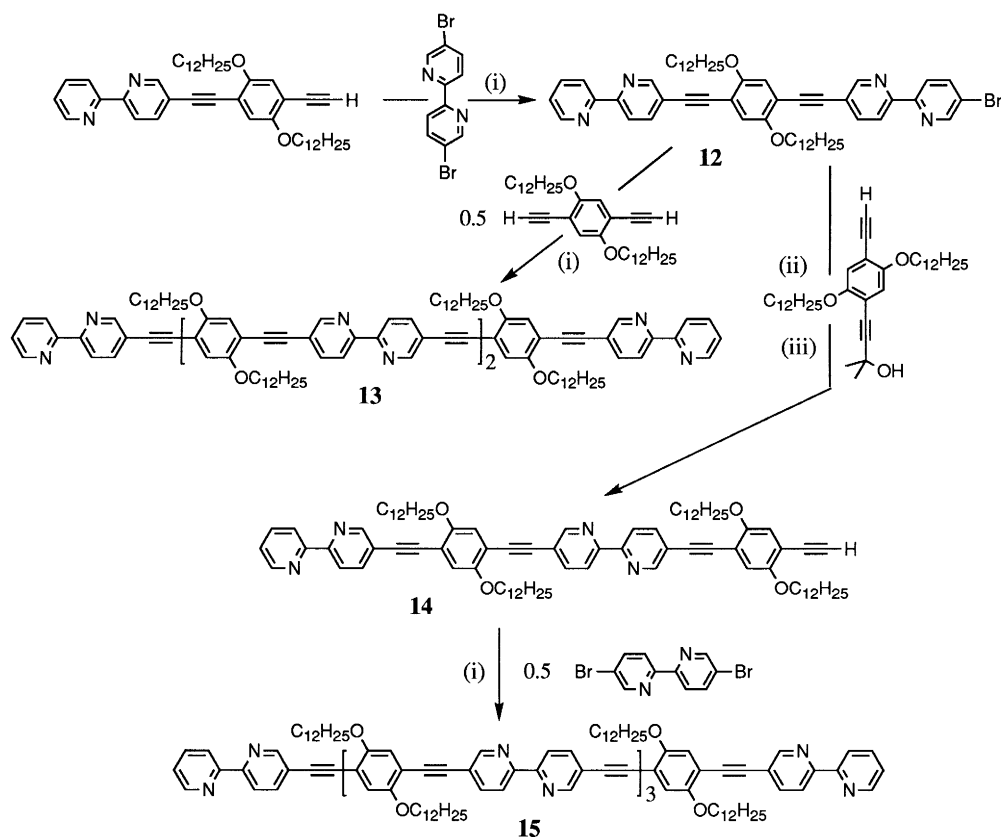
With these two intermediates in hand it was simple to prepare the soluble bis-bpy ligand **9** by double cross-coupling of derivative **8** with 5-bromo-bpy. Furthermore, access to the pivotal mono-bpy intermediate **10** allows us to synthesize, under mild conditions, the target tris-bpy ligand **11** in fair yield (Scheme 2).



Scheme 2. (i) n -PrNH₂, [Pd⁰(PPh₃)₄] (6 mol%), 70°C, 84% for **9**, 91% for **10** and 80% for **11**; (ii) NaOH (excess), benzene, 87%

This rational design has been extended to the construction of larger multitopic ligands. Here, the pivotal intermediates **12** and **14** were obtained as shown in Scheme 3 and allowed to react, under Pd-catalyzed conditions, with starting material **8** (0.5 equiv.) and 5,5'-dibromo-bpy to produce the tetra- and penta-bpy ligands **13** and **15**, respectively. It is worth pointing out that during the synthesis of derivative **12**, a side product assigned as the tritopic ligand **11** is formed by an inescapable double cross-coupling reaction. These desired products obtained in satisfactory yields were soluble in most chlorinated solvents, photostable and characterized by ¹H, ¹³C{¹H} NMR, FAB⁺-MS, UV-vis and IR spectroscopies. All data were consistent with the proposed structures (see Table 1 for selected analytical data). A typical NMR spectrum for compound **13** is given in Ref. 11.

In summary, we have presented a logical synthetic protocol for the synthesis of soluble segmented bipyridine-based ligands. At each stage of the procedure, key intermediates were prepared by either a selective or a complete deprotection reaction. One set of reaction conditions based on Pd(0)-catalyzed cross-coupling reactions is suitable for the entire iterative synthetic sequence. The ready availability of the reagents, the overall simplicity of the procedure, the use of mild reaction conditions, and the reasonable yields obtained, suggest that this methodology will be useful for the preparation of even more sophisticated scaffolds. The chemical- and photo-stability of these rigid-rod conjugated oligomers makes them very attractive for the construction of luminophoric d-block metal complexes where each metal subunit could act as a relay station in photon shuttling processes. We are currently exploring the coordinative properties of these multitopic ligands, to offer further insights into the chemistry of these interesting systems.¹²



Scheme 3. (i) $n\text{PrNH}_2$, $[\text{Pd}^0(\text{PPh}_3)_4]$ (6 mol%), 70°C , 76% for **12**, 76% for **13** and 71% for **15**; (ii) $n\text{PrNH}_2$, $[\text{Pd}^0(\text{PPh}_3)_4]$ (6 mol%), 70°C , 85%; (iii) NaOH (excess), benzene, 80°C , 84% for **14**

Table 1
Selected data for the novel poly-bipyridine ligands

Product	Yield (%) ^{a)}	m.p. ($^\circ\text{C}$)	IR (cm^{-1}) ^{b)}	UV-Vis λ nm, (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) ^{c)}	MS ^{d)}	$^{13}\text{C}\{^1\text{H}\}$ $\delta_{\text{C}\equiv\text{C}}$ (ppm) ^{e)}
9	84	105/6	2208	389 (13,700)	803.3	92.2; 92.1
11	80	139/40	2202	406 (22,000)	1450.2	92.2; 90.5; 90.2; 88.2
13	76	162/3	2203	408 (36,900)	2096.3	92.3; 92.2; 92.1; 90.5; 90.2; 89.8
15	75	179/8	2203	413 (39,900)	2743.5	92.2; 92.1; 90.6; 90.5; 87.4; 87.3; 83.9

a) Calculated for the final cross-coupling step; b) $\nu_{\text{C}\equiv\text{C}}$ stretching vibration measured in KBr pellets; c) less energetic absorption band measured in CH_2Cl_2 ; d) obtained by FAB⁺ using *meta*-nitrobenzyl alcohol as matrix and corresponds to $[\text{M}+\text{H}]^+$; e) in CDCl_3 .

Acknowledgements

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9. Ligand **4**: mp >300°C; FAB⁺ *m/z* 691.2 [M+H]⁺; FT-IR (KBr, cm⁻¹) 3049 (m), 2977 (m), 2200 (w, ν_{C≡C}), 1589 (m), 1569 (m), 1542 (m), 1465 (s), 1434 (m), 1368 (m), 1022 (m), 840 (s), 796 (s), 738 (s). Anal. calcd for C₄₆H₂₆N₈: (Mr=690.773); C 79.98, H 3.79, N 16.22; found: C 79.61, H 3.72, N 15.86; Ligand **5**: mp >300°C; FAB⁺ *m/z* 869.4 [M+H]⁺; FT-IR (KBr, cm⁻¹) 3050 (m), 2979 (m), 2216 (w, ν_{C≡C}), 1590 (m), 1467 (s), 1439 (m), 1375 (m), 1032 (m), 799 (s), 742 (s). Anal. calcd for C₅₈H₃₂N₁₀: (Mr=868.968); C 80.17, H 3.71, N 16.12; found: C 79.80, H 3.49, N 15.89.
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11. ¹H NMR (CDCl₃, 20°C) for ligand **13**: δ 8.83 (s, 6H), 8.69 (d, ³J_{H-H}=4.8 Hz, 2H), 8.44 (m, 8H), 7.94 (dd, ³J_{H-H}=8.4 Hz, ⁴J_{H-H}=1.9 Hz, 6H), 7.84 (td, ³J_{H-H}=7.5 Hz, ⁴J_{H-H}=1.6 Hz, 2H), 7.33 (td, ³J_{H-H}=7.5 Hz, ⁴J_{H-H}=1.9 Hz, 2H), 7.07 (s, Ph, 6H), 4.07 (t, ³J_{H-H}=6.2 Hz, OCH₂, 12H), 1.89 (m, CH₂, 12H), 1.24 (m, CH₂, 108H), 0.87 (m, CH₃, 18H).
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