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Homoditopic Platforms

Synthesis of Homoditopic Ligands with an Incrementable Rodlike Backbone

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Abstract: We describe the synthesis of architectures that consist of a symmetrical rodlike oligo(phenylene-ethynylene) (OPE) backbone of incrementable length connected to a pair of classical ligands for metal coordination. OPE spacers decorated with various end groups and incorporating up to seven phenylene-acetylene repeat units were quickly obtained through a bidirectional approach. Efficient further functionalization with useful coordinating groups were achieved. The resulting homoditopic platforms are of interest in numerous fields ranging from supramolecular chemistry to materials science.

Introduction

Ditopic ligands, that is, ligands that possess two distinct coordination sites,[1] are widely employed building blocks as they can lead to well-ordered supramolecular assemblies when coordinated to metal cations.[2] Starting from very simple molecules, complex and aesthetic architectures that display unusual properties can be easily obtained through coordination-driven self-assembly.[3] Hence, an impressive number of discrete metallacycles or cages have been prepared since the pioneering work of Lehn[4] and Sauvage.[5] In these molecular edifices, the ditopic ligands often consist of two coordinating moieties connected to a rigid rodlike backbone. These "struts" can play the role of pillars in host–guest coordination cages[6] or organic linkers in metal–organic frameworks (MOFs),[7] but they have numerous applications. For instance, metal complexes of bis-terpyridines can form discrete dyads that can act as molecular devices.[8] Dinuclear lanthanide or Mn^{II} complexes of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) and its counterpart missing an acetate arm (DO3A) linked through an aromatic spacer have also proved useful as contrast agents in magnetic resonance imaging (MRI)[9–11] and molecular recognition[12,13] due to their luminescent properties[14,15] as well as in model systems in which the spin–spin distances were measured by using pulsed electron paramagnetic resonance (EPR) methods.[16–19]

The generation of ditopic platforms incorporating two ligands connected to a central rigid molecular wire of incrementing length is needed for diverse applications. This has been achieved with bis-terpyridine (bis-Tpy) oligomers with ethynylthiophene,[20] ethynylnaphthalene[21] or phenylene-ethynylene[22–24] repeat units. Oligo(phenylene-ethynylene) (OPE) spacers[25–29] of incrementing length spin-labelled with Gd^{III} complexes of the ligand PyMTA (pyridine methylenediamine tetraacetate), a derivative of dipicolinic acid (DPA), have also been synthesized to act as molecular rulers for EPR-based distance measurements.[30,31] Such systems, in which the ligand–ligand distance can be easily tailored, are also very useful for controlling the size of host–guest cavities or the porosity of MOFs.[32]

In this paper we describe an efficient strategy for building systems incorporating a central incrementable OPE rod connected at both ends to a Tpy, PyMTA, DPA, DO3A or DOTA ligand. First, we present a method to rapidly generate OPE linkers with various end groups and then describe efficient techniques to graft the aforementioned ligands. Discrete OPE oligomers with up to 16 phenylene-acetylene repeat units, equipped with diverse solubilizing moieties, have been prepared by using different strategies that have been recently reviewed.[33] We have chosen the so-called bidirectional approach,[34,35] which is well suited to the synthesis of symmetrical OPE linkers. To improve its efficiency, we decided to derivatize only one phenyl ring out of two with small poly(ethylene glycol) (PEG) chains so that the OPE spacer can be quickly elongated (four repeat units added in one step) while maintaining good solubility in organic solvents. This methodology is very convergent as all the building blocks can be obtained in only a few synthetic steps and OPE linkers with five or seven repeat

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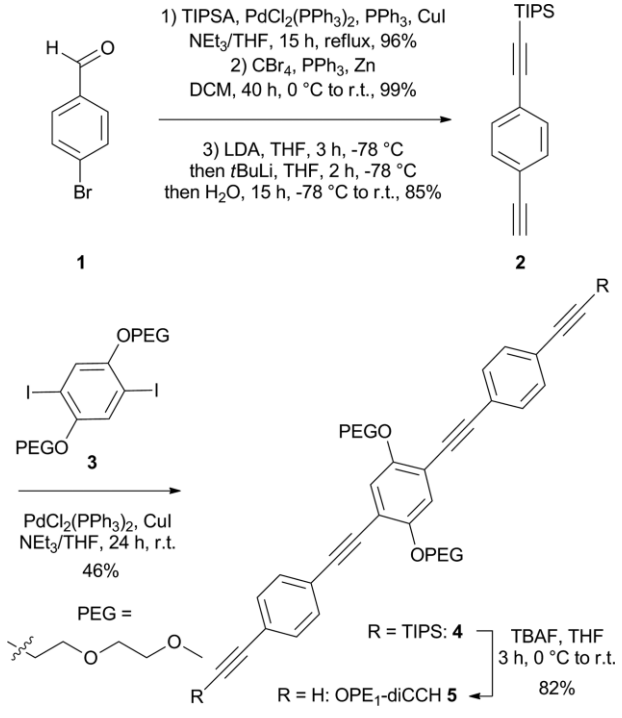
units (i.e., up to 4.7 nm) are generated with the longest linear sequence of five or six steps, respectively.

Results and Discussion

The central diethynyl building block was synthesized starting from commercially available *p*-bromobenzaldehyde (**1**), which was converted into the monoprotected diethynylbenzene **2** in three steps (global yield: 81 %) according to a Sonogashira/Corey–Fuchs sequence described by Nierengarten et al. with slight modifications.[36] Indeed, under the conditions described, a mixture of the desired alkyne **2** and the corresponding bromoalkyne was obtained. The use of *t*BuLi as a stronger base than LDA (for definitions of reagents, see the Experimental Section) was necessary to convert the remaining bromoalkyne into compound **2**. This intermediate was then engaged in a Sonogashira reaction with the diiodo building block **3**, synthesized in three steps under conditions previously described,[18] to afford the expected coupling product **4**. Compound **4** was deprotected with TBAF to give the OPE linker **5** equipped with ethynyl end groups in gram amounts (Scheme 1). Its structure was confirmed by X-ray crystallography, as yellow needles of OPE_1-diCCH **5** were obtained by slow evaporation from a 1:1 toluene/DCM mixture (Figure 1A). This compound crystallizes in the $P2_1$ space group (monoclinic system), with two molecules per asymmetric unit.



Scheme 1. Synthesis of OPE-diCCH **5**.

Under the same conditions, OPE linkers **6** and **7** were synthesized from compound **3** and 2.0 equiv. of the corresponding *p*-ethynylbenzene equipped with an amine (commercially available) or an aldehyde group (synthesized in two steps), as described previously.[18] Similarly, the iodinated coupling partners **8** and **9** were obtained by a mono-Sonogashira reaction between compound **3** and 0.75 equiv. of the corresponding *p*-ethynylbenzene, with limited formation of the dicoupled product (between 5 and 10 %). Compounds **8** and **9** were then engaged in a double Sonogashira coupling reaction with either commercially available *p*-diethynylbenzene or OPE linker **5** to obtain the corresponding linkers **10**–**13** in moderate-to-good yields (Scheme 2).

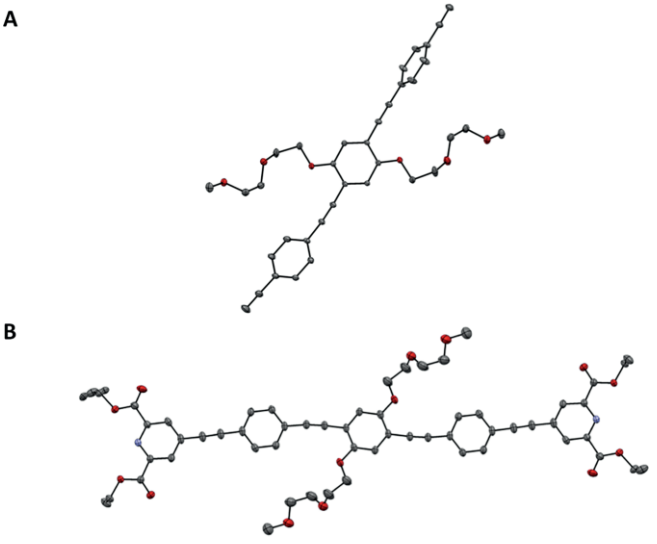
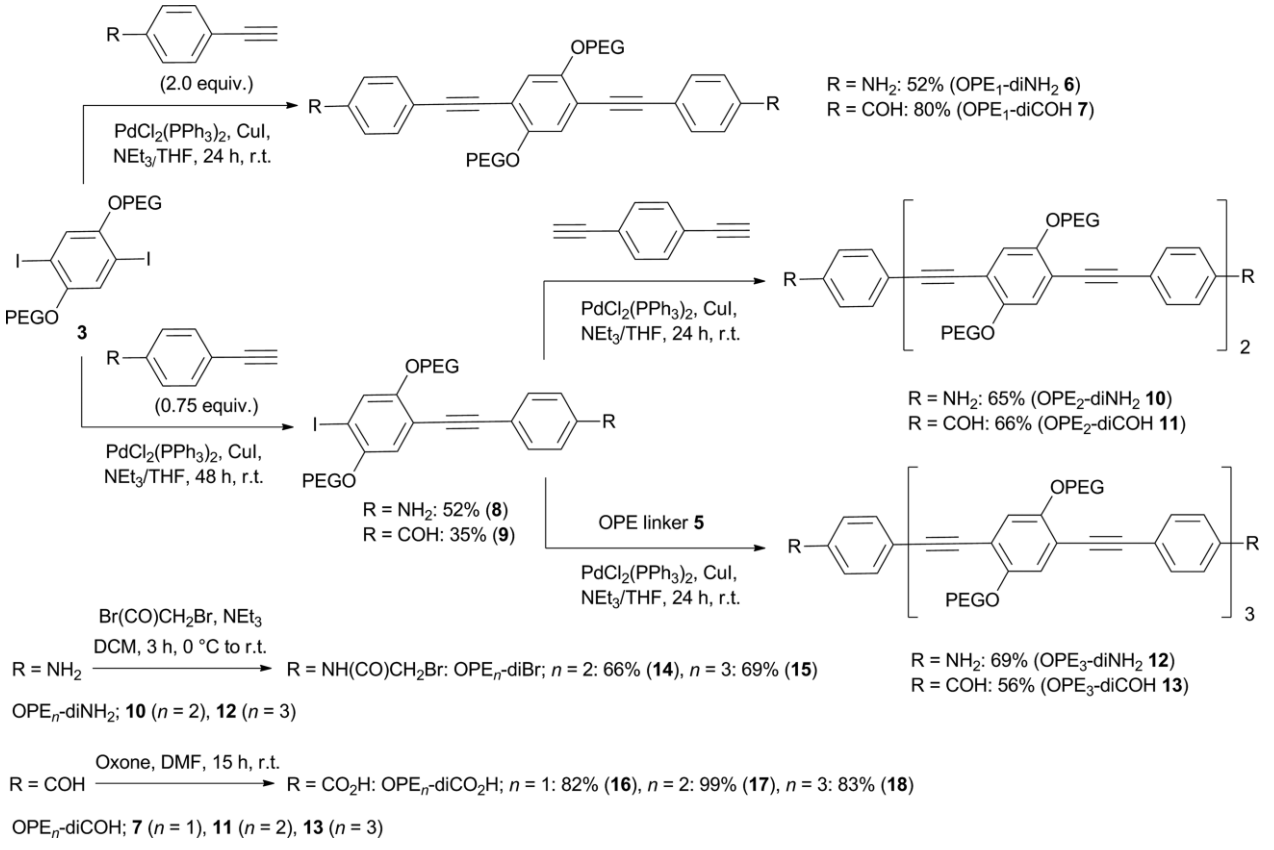


Figure 1. ORTEP drawings of (A) OPE_1-diCCH **5** and (B) tetraester **23**. Hydrogen atoms have been omitted for clarity; ellipsoids are drawn at probability levels of 50 %.

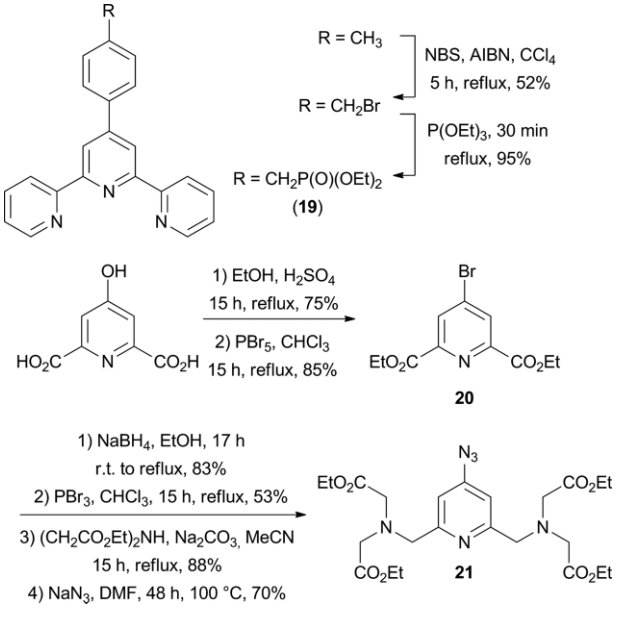
Other useful functional groups can be generated. The reactions of compounds **10** and **12** with bromoacetyl bromide in the presence of NEt_3 gave products **14** and **15**, respectively, equipped with a CH_2Br moiety, which can react further with various modules through nucleophilic substitution reactions.[18] Compounds **7**, **11** and **13** were oxidized to the corresponding carboxylic acids **16**, **17** and **18** in nearly quantitative yields by using Oxone in DMF, as described previously for the corresponding shorter OPE spacer (Scheme 2).[18]

OPE linkers **6**, **7** and **10**–**18** were subsequently used for the synthesis of homoditopic platforms. To illustrate the diversity of the possible functionalizations, a selection of the described OPE linkers were chosen to react with selected ligands. Terpyridine **19** equipped with a phosphonate group was synthesized in two steps starting from *p*-tolyl-terpyridine by a radical bromination with *N*-bromosuccinimide (NBS) and azobis-isobutyronitrile (AIBN) followed by an Arbuzov reaction with $P(OEt)_3$, according to a procedure described by Winter et al.[37] The diethyl ester of DPA **20**, incorporating a bromo group in the *para* position, was obtained from chelidamic acid by esterification and bromination with PBr_5 following a procedure of Takalo et al.[38] According to the same procedure, reduction of the ester moieties with $NaBH_4$ followed by bromination with PBr_3 gave the corresponding tribrominated product. Reaction with ethyl iminodiacetate and substitution with sodium azide, as described by Tóth and co-workers, afforded the tetraethyl ester of PyMTA **21** equipped with an azido moiety (Scheme 3).[39]

A double Horner–Wadsworth–Emmons reaction between terpyridine **19** and OPE_1-diCOH **7** in the presence of NaH af-



Scheme 2. Synthesis of compounds **6**, **7** and **10**–**18**.

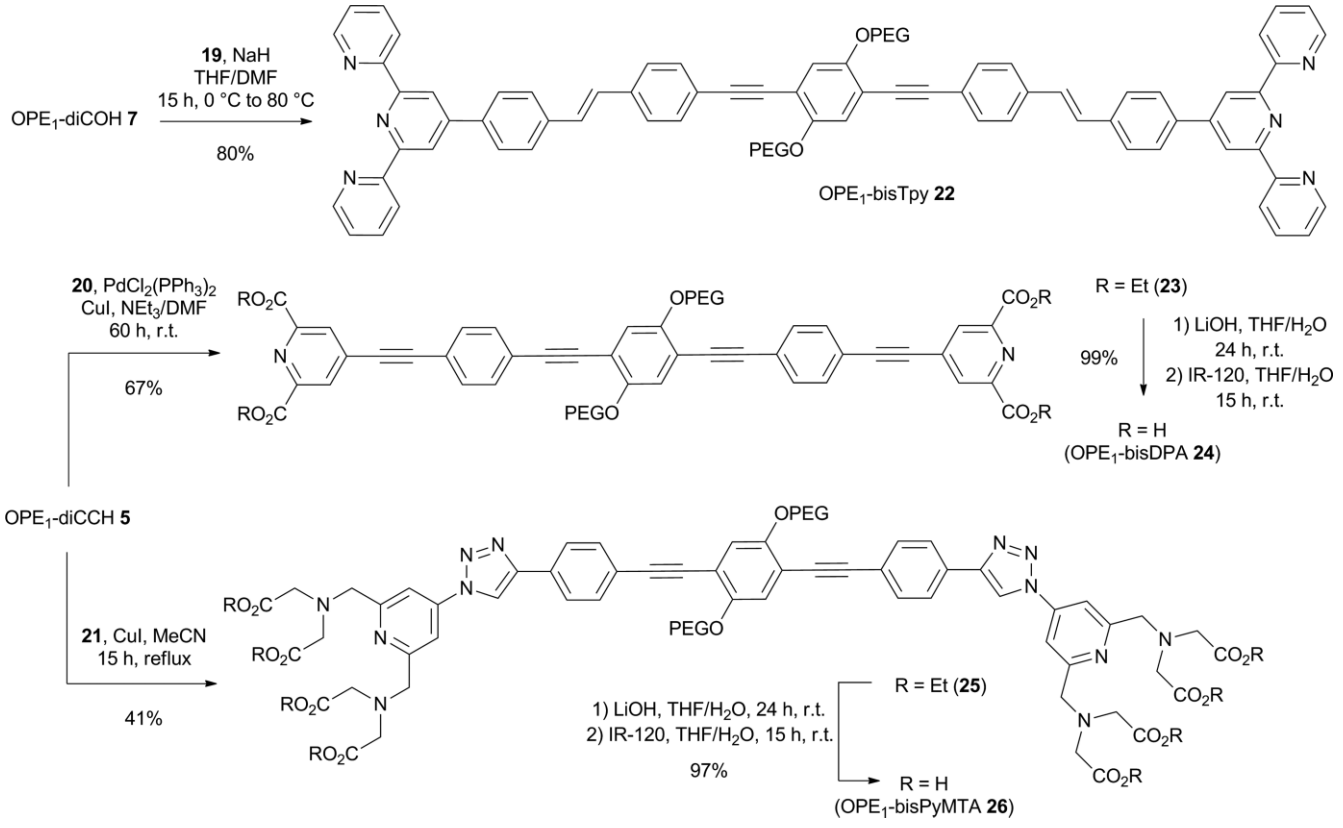


Scheme 3. Synthesis of pyridine derivatives **19**–**21**.

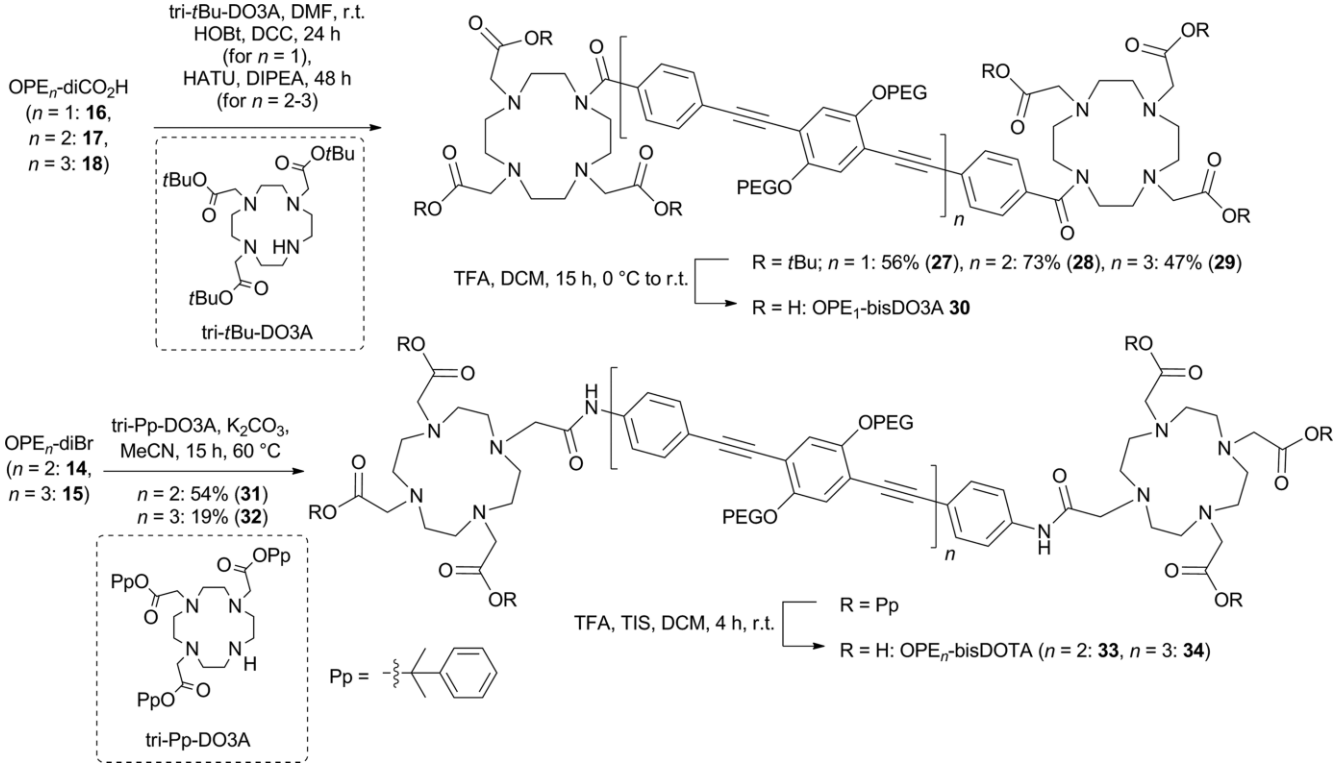
forded the corresponding OPE$_1$-bisTpy **22** in good yield (80 %; Scheme 4). The use of KO*t*Bu, as recommended by Winter et al.,[37] led to the recovery of the reactants. Next, a Sonogashira coupling between the diethyl ester of DPA **20**[38] and OPE$_1$-diCCH **5** in NEt$_3$/DMF generated the corresponding product **23**. Noteworthy, the use of NEt$_3$/THF as solvent at reflux led to decomposition, whereas no reaction was observed at room temperature in the same solvent due to the poor solubility of the reactants. The structure of tetraester **23** was confirmed by X-ray crystallography: yellow crystals were grown from a deuteriated chloroform solution. This molecule crystallizes in the $P\bar{1}$ space group (triclinic system) with one of the ethyl groups being slightly disordered. In contrast to linker **5**, the five aromatic rings are nearly coplanar: parallel sheets form in the packing unit due to a combination of π stacking and hydrogen bonds (Figure 1B).

The OPE$_1$-bisDPA platform **24** was then obtained in nearly quantitative yield by ethyl ester hydrolysis with LiOH followed by treatment with ion-exchange resin Amberlite IR-120. Finally, PyMTA tetraester **21** and linker **5** were connected by click chemistry using CuI in MeCN, as proposed by Tóth et al.,[39] to give octaester **25**, which was deprotected to afford the OPE$_1$-bisPyMTA module **26** (Scheme 4).

The dicarboxylic acid terminated OPE linkers can be functionalized through amidation reactions. Compounds **16**–**18** were treated with commercially available tri-*t*Bu-DO3A in the presence of HOBt and DCC or HATU as coupling agents to afford the protected platforms **27**–**29**. The smallest hexaester **27** was then deprotected with TFA to give the bisDO3A module **30** after HPLC purification. Finally, to illustrate the diversity of the functionalization methods available with these OPE linkers, compounds **14** and **15** were treated with the previously reported tri-Pp-DO3A[18] to give platforms **31** and **32**. The 2-phenylisopropyl (Pp) groups were deprotected with 2 % TFA



Scheme 4. Synthesis of OPE_1-bisTpy **22**, OPE_1-bisDPA **24** and OPE_1-bisPyMTA **26**.



Scheme 5. Synthesis of bisDO3A **30** and bisDOTAs **33**–**34**.

in DCM to afford bisDOTA compounds **33** and **34** after HPLC purification (Scheme 5).

Coordination chemistry studies of the described ditopic ligands will be performed with various transition-metal ions. In

preliminary experiments, the reaction of OPE_1-bisDPA **24** with $Mn(ClO_4)_2 \cdot 6H_2O$ (2.5 equiv.) in a mixture of THF and H_2O (1:1) afforded a yellow precipitate, the very low solubility of which in classical solvents precluded any further investigation. The reaction of OPE_1-bisPyMTA **26** with $MnCl_2$ (2.5 equiv.) at controlled pH afforded the expected bis-Mn complex as a yellow solid (as shown by mass spectroscopy, see the Supporting Information), which was soluble in water at pH 8. In the DO3A/DOTA series, the formation of the bis-Mn complex of OPE_1-bisDOTA compound was also attested by mass spectroscopy.[18]

Conclusions

Various systems consisting of a pair of ligands connected through an OPE wire of incrementing length have been efficiently synthesized. The methodology employed in this work is quick, convergent and provides linkers with various end groups that can be easily further functionalized with useful ligands. Such architectures could easily find applications in numerous domains, from supramolecular chemistry to materials science. The coordination chemistry of the ditopic ligands described herein is currently being explored with various transition-metal ions and the resulting homodinuclear complexes will be studied for their properties in different fields such as pulsed EPR-based distance measurements and coordination-driven self-assembly. Further investigations, such as the characterization of the conductance of the OPE rods and of the electronic communication between metal centres in selected complexes and analysis of their mixed-valence character, would be of high interest. Finally, adaptation of the methodology to the efficient synthesis of disymmetrized heteroditopic ligands is currently being investigated.

Experimental Section

General: Unless otherwise stated, all syntheses were performed under inert atmosphere (argon or nitrogen). Reagents and chemicals were used without further purification. Dry solvents [dichloromethane (DCM), MeCN, THF, dioxane, dimethylformamide (DMF)] were purchased from commercial sources and used without further purification. Triethylamine (TEA) was dried with CaH_2, distilled under argon and stored over 4 Å molecular sieves under argon. Preparative column chromatography was carried out with silica gel (Si 60, 40–63 μm) unless otherwise stated. Analytical TLC analysis was carried out on silica gel (60F-254) with UV visualization at 254 and 366 nm. Analytical HPLC measurements were performed with a Dionex Ultimate 3000 instrument using C18A ACE columns. Preparative HPLC was performed with a Waters 600 instrument using an XBridgeTM Prep C18 OBDTM column. Gradients of MeCN in H_2O, both containing 0.1 % TFA, were employed. Products were monitored by UV detection. ^1H and ^{13}C NMR spectra were recorded with a 300 MHz spectrometer at Ecole Normale Supérieure (ENS) in the Laboratoire des Biomolécules (LBM, UMR 7203) with solvent residuals as internal references [$CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR; $(CD_3)_2SO$: 2.50 ppm for ^1H NMR and 39.52 ppm for ^{13}C NMR]. The following abbreviations are used: singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br.). Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) in Hz. HRMS using electrospray ionization (ESI) was performed at the Université Paris Sud in the Service de Spectrométrie de masse of the ICMMO (Institut de Chimie Moléculaire et des Matériaux d'Orsay). ESI-HRMS was also performed at UPMC (IPCM). Tpy ligand **19** and ethyl esters of DPA **20** and PyMTA **21** were synthesized as described previously.[37–39] *p*-Ethynylbenzaldehyde, tri-Pp-DO3A, linkers OPE_1-diNH_2 **6**, OPE_1-diCOH **7** and OPE_1-diCO_2H **16** were synthesized as described previously by us.[18] The following abbreviations are used: Cy (cyclohexane), DCC (*N*,*N*′-dicyclohexylcarbodiimide), DIPEA (*N*,*N*′-diisopropylethylamine), DO3A (1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid), DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid), EDTA (ethylenediaminetetraacetic acid), HATU {1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-*b*]pyridinium 3-oxide hexafluorophosphate}, HOBt (*N*-hydroxybenzotriazole), LDA (lithium diisopropylamide), OPEG (diethylene glycol monomethyl ether), TBAF (tetra-*n*-butylammonium fluoride), TEA (triethylamine), TFA (trifluoroacetic acid).

General Procedure A — Mono-Sonogashira Coupling: $Ph(OPEG)_2I_2$ (**3**; 1.0 equiv.) and *p*-ethynylaniline or *p*-ethynylbenzaldehyde (0.75 equiv.) were dissolved in a mixture of dry THF and dry TEA. Argon was bubbled through the solution for 15 min and then $[PdCl_2(PPh_3)_2]$ (0.1 equiv.) and CuI (0.2 equiv.) were added. The resulting suspension was stirred at room temp. for 48 h, a sat. aq. solution of NH_4Cl was added and the mixture was extracted with DCM (3 ×). The combined organic layers were dried with Na_2SO_4, filtered and concentrated. Column chromatography afforded the corresponding products **8** and **9**.

General Procedure B — Bis-Sonogashira Coupling: Iodide **8** or **9** (1.0 equiv.) and diyne **5** or *p*-diethynylbenzene (2.0 equiv.) were dissolved in a mixture of dry THF and dry TEA. Argon was bubbled through the solution for 15 min and then $[PdCl_2(PPh_3)_2]$ (0.1 equiv.) and CuI (0.2 equiv.) were added. The resulting suspension was stirred for 24 h at room temp., a sat. aq. solution of NH_4Cl was added and the mixture was extracted with DCM (3 ×). The combined organic layers were dried with Na_2SO_4, filtered and concentrated. Column chromatography afforded the corresponding OPE linkers **10**–**13**.

General Procedure C — Synthesis of Dibromo OPE Linkers 14 and 15: Linker **10** or **12** (1.0 equiv.) was dissolved in dry DCM. The resulting solution was cooled to 0 °C, and TEA (2.5 equiv.) was added, followed by bromoacetyl bromide (2.5 equiv.) dissolved in dry DCM dropwise. The resulting mixture was warmed to room temp. for 3 h and washed with a sat. aq. solution of $NaHCO_3$ (1 ×) and a sat. aq. solution of NaCl (1 ×). The organic layer was dried with Na_2SO_4, filtered and concentrated. Column chromatography afforded the corresponding dibromo OPE linkers **14** and **15**.

General Procedure D — Synthesis of Dicarboxylic OPE Linkers 17 and 18: Linker **11** or **13** (1.0 equiv.) was suspended in dry DMF. $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (Oxone®, 2.0 equiv.) was added and the resulting suspension was stirred at room temp. for 15 h. H_2O was added and the resulting precipitate was filtered, washed with H_2O, taken up in acetone and dried to afford the corresponding dicarboxylic OPE linkers **17** and **18**.

General Procedure E — Synthesis of *t*Bu-Protected Bis-DO3A Compounds 28 and 29: Linker **17** or **18** (1.0 equiv.) and HATU (2.2 equiv.) were dissolved in dry DMF and stirred at room temp. for 10 min. Tri-*t*Bu-DO3A (2.5 equiv.) was added and the resulting mixture was stirred at room temp. for 20 min. DIPEA (6.0 equiv.) was added and the resulting mixture was stirred at room temp. for 48 h and concentrated. The residue was taken up in DCM, washed

with H_2O (1 ×) and a sat. aq. solution of NaCl (1 ×), dried with Na_2SO_4, filtered and the solvents evaporated. Column chromatography afforded the corresponding *t*Bu-protected bisDO3A compounds **28** and **29** as yellow sticky solids.

General Procedure F — Synthesis of Pp-Protected BisDOTA Compounds 31 and 32: Linker **14** or **15** (1.0 equiv.) and tri-Pp-DO3A (2.5 equiv.) were mixed in dry MeCN. K_2CO_3 (10.0 equiv.) was added and the resulting mixture was heated at 60 °C for 15 h and concentrated. DCM was added and the mixture was washed with H_2O (1 ×) and a sat. aq. solution of NaCl (1 ×), dried with Na_2SO_4, filtered and concentrated. Column chromatography afforded the corresponding Pp-protected bisDOTA compounds **31** and **32** as yellow solids.

General Procedure G — Deprotection of Pp-Protected BisDOTA Compounds: Pp-protected bisDOTA compound **31** or **32** was dissolved in a mixture of TFA/TIS/DCM (2:2:96, 10 mg mL^{-1}). The resulting solution was stirred at room temp. for 4 h and concentrated. MeOH was added, and the product was precipitated by the slow addition of Et_2O, filtered and dried. The crude product was purified by preparative HPLC to afford the corresponding OPE-bisDOTA linkers **33** and **34** as yellow solids.

X-ray Crystallography: X-ray diffraction data for compound **5** was collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo-K_α radiation. A crystal was mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flash frozen in a stream of nitrogen gas at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentzian, polarization and absorption effects. The structures were solved by direct methods with SHELXS-97[40,41] and refined against F^2 by full-matrix least-squares techniques with SHELXL-2014[42] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WinGX.[43]

Yellow stick-like crystals of compound **23** suitable for X-ray crystallography were obtained from a deuteriated chloroform solution. A single crystal of the compound was selected, mounted onto a CryoLoop and transferred in a cold stream of nitrogen gas. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with Cu-K_α radiation (λ = 1.54178 Å). Data collection was performed with the APEX2 suite (Bruker).[44] Unit cell parameter refinement, integration and data reduction were carried out with the SAINT program (Bruker).[44] SADABS (Bruker) was used for scaling and multi-scan absorption corrections. In the WinGX suite of programs,[43] the structure was solved by using the SHELXT[45] program and refined by full-matrix least-squares methods with SHELXL-2014.[42] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined with a riding model. A model of disorder was introduced for a terminal ethyl chain. The crystal data collection and refinement parameters are given in Table S1 in the Supporting Information.

CCDC 1484299 (for **5**) and 1485975 (for **23**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Ligand design · N ligands · Synthetic methods · Rigid spacers · Supramolecular chemistry

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