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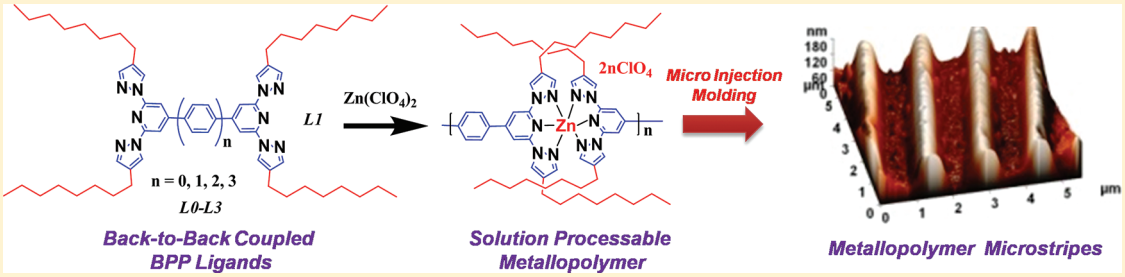
Micropatterning of Metallopolymers: Syntheses of Back-to-Back Coupled Octylated 2,6-Bis(pyrazolyl)pyridine Ligands and Their Solution-Processable Coordination Polymers

Supratim Basak, Pramiti Hui, Sathyanarayana Boodida, and Rajadurai Chandrasekar*

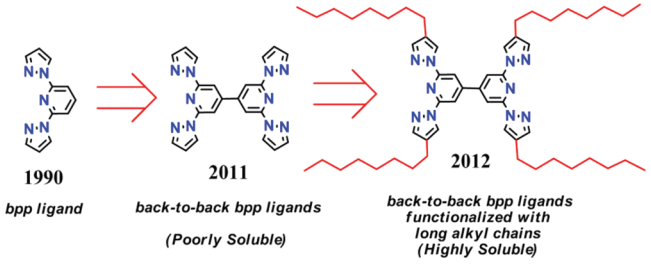
Functional Molecular Nano/Micro Solids Laboratory, School of Chemistry, University of Hyderabad, Prof. C. R. Rao Road, Gachi Bowli, Hyderabad-500046, India

Supporting Information



ABSTRACT: This paper presents a 10-step synthetic route for the preparation of a series of new back-to-back coupled 2,6-bis(pyrazol-1-yl)pyridine (bpp) ligands (***L0–L3***) decorated with tetraoctyl chains. Ligand ***L1*** self-assembles with Zn^{2+} ion to form a highly soluble metallo-supramolecular polymer **1** with $M_n \sim 9600$ g/mol. To demonstrate the processability of polymer **1**, by following a "top-down" approach periodic one-dimensional fluorescent microstripes were fabricated on a silica substrate.

The design and synthesis of heterocyclic tridentate ligand molecules have attracted significant attention in recent years due to their imperative role they play in biology, medicine, chemistry, materials science, and nanoscience and technology.[1−9] In particular, the challenge lies in the synthesis of novel heterocyclic ditopic ligand molecules which can form metallo-supramolecular polymers (MSPs) having good solubility and high molecular weight. To obtain better solution processability for practical applications, mostly MSPs were synthesized by using appropriate combination of ligands, counterions, and organic polymeric units into the main or side chain of the polymers. Mostly, modified benzimidazole-,[2] terpyridine-,[3−6] and bistriazolylpyridine-type[7,8] ligands were exploited for this purpose.



A recent addition to the club of functional MSPs is derived from a back-to-back coupled 2,6-bis(pyrazolyl)pyridine (bpp)[9,10] molecule with phenyl spacer. This molecule forms magnetically bistable spin crossover 1-D MSP with iron(II) ions.[9a] Unfortunately, the obtained low molecular weight MSP is not processable for any device fabrication because of its poor solubility in most of the organic solvents. In this context, the design and synthesis of well-alkylated ditopic bpp ligands for the preparation of solution-processable MSPs is necessary for a straightforward device fabrication.

In this paper, for the first time, we report our novel methodology for the synthesis of a series of π-conjugated back-to-back coupled tetraoctylated bpp ligands ***L0–L3*** connected by different aromatic spacers (no bridging unit (***L0***), with phenyl (***L1***), with biphenyl (***L2***), and with terphenyl (***L3***) bridging units, respectively). In addition, to demonstrate the use of these soluble ligands, we report the preparation of a highly soluble 1-D MSP $[\mathbf{L1}\cdot Zn(ClO_4)_2]_n$ **1** having molecular weight $M_n \sim 9{,}600$ g/mol from ***L1*** and Zn^{2+} ion. Following top-down approach, by utilizing the good solubility of **1** in many organic solvents, fabrication of several millimeters long of microstrips of width in the range of 600−700 nm using microinject molding technique is also presented. We also provide the detail characterization of microstrips by using field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and Raman imaging/spectroscopy.

For the synthesis of ***L0–L3*** molecules, a novel 10-step synthetic protocol from the low-priced citrazinic acid was developed (Scheme 1, route 1). Transformation of citrazinic acid into 2,6-dichloroisonicotinicacidmethyl ester **2** and its subsequent conversion into **3** was effected as per the reported

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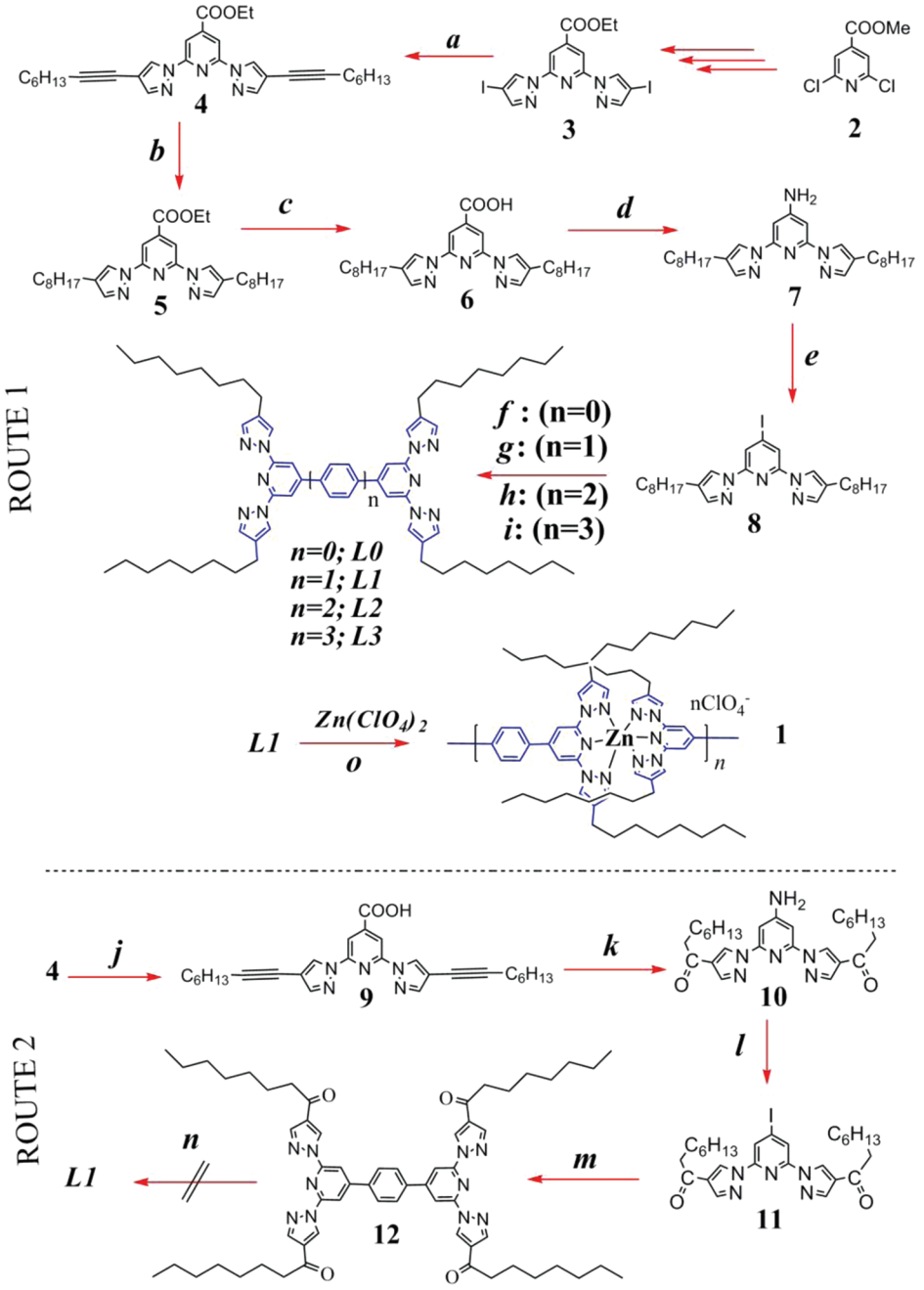
Scheme 1[a]



[a]Reagents and conditions: (a) 1-octyne, CuI, $Pd(PPh_3)_2Cl_2$, PPh_3, dioxane/TEA; (b) Pd/C, H_2; (c) LiOH/THF/HCl; (d) oxalyl chloride ($C_2O_2Cl_2$)/NaN_3/TFA/K_2CO_3; (e) $NaNO_2$/HCl/aqueous KI; (f–i) Suzuki conditions: Na_2CO_3/1,4-dioxane/3 d/70 °C; (f) bispinacolato diborane; (g) 1,4-phenyldiboronic acid; (h) 4,4′-biphenyldiboronic acid; (i) 4,4″-triphenyldiboronic acid; (j) LiOH/THF/HCl (2 N); (k) $C_2O_2Cl_2$ /NaN_3/TFA/K_2CO_3; (l) $NaNO_2$/HCl/aqueous KI; (m) 1,4-phenylenebisboronic acid/1,4-dioxane/Na_2CO_3/3 d/70 °C; (n) NH_2–NH_2/KOH/diethyleneglycol/180 °C/2 d; (o) $Zn(ClO_4)_2$/DCM/MeOH.

procedures.[10,11] Attachment of 1-octyne to the 4- and 4″-carbon of the pyrazole unit in bpp of **3** was successfully carried out under Sonogashira cross-coupling conditions to get **4** in 82% yield. The alkyne groups in **4** was reduced using Pd/C under H_2 atmosphere to obtain highly soluble 2,6-dioctyl precursor **5** in a quantitative 99% yield. The saponification reaction quantitatively converted compound **5** into its carboxylic acid derivative **6** in 98% yield. Furthermore, sequential conversion of the carboxylic acid **6** into acyl azide followed by a thermal Curtius rearrangement and succeeding hydrolysis of the trifluoroacetamide provided the amino derivative **7** in 78% yield. From this compound **7**, a key intermediate dioctylated 4-iodo bpp derivative **8** was synthesized in a modest 34% yield by using isoamylnitrite in presence of KI and I_2. Treatment of compound **8** with bispinacolato diborane under Suzuki cross-coupling condition formed a directly back-to-back coupled dioctylated bpp ***L0*** in a decent 72% yield. Similarly, Suzuki cross-coupling reactions of compound **8** with 1,4-phenyldiboronic acid, 4,4′-biphenyldiboronic acid[12] (**13**), and 4,4″-triphenyldiboronic acid[12] (**14**) provided the other target

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molecules ***L1***, ***L2***, and ***L3***, respectively, in ca. 70−90% yield. Earlier, in an another alternative method (route 2), saponification of **4** yielded **9**, which upon subsequent Curtius rearrangement converted the alkyne bonds to carbonyl group to give **10** due to the use of strong trifluoroacetic acid.[13] Transformation of **10** to **11** is effective. Later under Suzuki coupling **11** gave a back-to-back coupled ligand **12** with four octyl chains containing carbonyl groups. Unfortunately, reduction of the carbonyl groups in **12** to synthesis ***L1*** was unsuccessful under Wolff−Kishner reduction conditions.

The UV−vis absorption studies of ***L0−L3*** in dichloromethane (DCM) displayed absorption maxima (λ_{max}) at 334, 292, 313, and 321 nm, respectively (Figure S1, Supporting Information) (Table 1). All ligands ***L0−L3*** in DCM showed a violet fluorescence with emission maxima (λ_{max}) at 457, 394, 388, and 401 nm, respectively. The quantum yields (Φ_f) of ***L0−L3*** are in the following order: 0.78, 0.22, 0.60, and 0.62, respectively. In the solid state (powder, crystalline), ligands ***L1−L3*** displayed a violet fluorescence upon irradiated with 365 nm UV light.

Table 1. Photophysical Properties of *L1−L3* in Dichloromethane

compd	λ_{abs} (nm) (ε) (M^{-1} cm^{-1})	$\lambda_{emission}$ (nm)	Φ_f[a]
L0	255 (48777); 290 (33771); 334 (17923)	457	0.779
L1	228 (16187); 258 (26700); 292 (32173)	394	0.217
L2	229 (22444) ; 259 (32753); 313 (41933)	388	0.60
L3	229(34435); 259 (41350); 321(61204)	401	0.62

[a]Quinine sulfate as reference (Q_{ref} = 0.577).

In order to prepare a highly soluble 1D metallo-supramolecular polymer, ***L1*** was self-assembled with $Zn(ClO_4)_2$ (1:1 ratio) to get a coordination polymer $[L1{\cdot}Zn(ClO_4)_2]_n$ **1**. Complexation of the metal ion to the ligand was followed by UV−vis, fluorescent, and NMR spectroscopy titration studies. In UV−vis studies, upon addition of Zn^{2+} ion to ligand ***L1*** (1:1 ratio) the intensity of the ligand absorption band at 292 nm decreased sharply with broadening of the band (Figure 1) due to the formation of a linear chain of six coordinated Zn(II) complex.[14] Furthermore, the steady-state fluorescence spectra showed a sharp decrease in the fluorescence intensity accompanied by a 14 nm bathochromic shift of the free ligand (***L1***) fluorescent signal upon reaching the 1:1 stoichiometry of ***L1*** and Zn^{2+}, with no change in the intensity upon further addition of metal ion (Figure 1). The plot of extinction and the Zn/***L1*** ratio showed a linear decrease and a sharp end point at a metal/ligand ratio of 1:1, indicating the formation of a 1:1 $[L1{\cdot}Zn(ClO_4)_2]_n$ complex **1**.

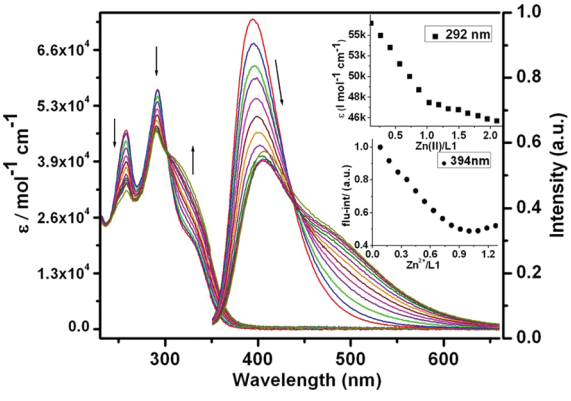

Figure 1. UV−vis and fluorescence titration spectra of ligand ***L1*** with $Zn(ClO_4)_2$ in dichloromethane at 25 °C; the top inset shows the plot of molar extinction coefficient of 292 nm band as a function Zn(II) ion to ***L1*** ratio; the bottom inset shows the plot of change in the fluorescence intensity at 394 nm, as a function of Zn(II) ion to ***L1*** ratio. Arrows indicate the spectral changes with increasing amounts of Zn(II) ions.

Fluorescence anisotropy titration showed an increase in anisotropy from 0.011 (for free ***L1***) to 0.021 upon addition of one equivalent Zn(II) perchlorate (Figure S2, Supporting Information). Further increase of concentration of Zn^{2+} showed a sluggish decrease in anisotropy value suggesting a decrease in polymer chain length which is also evident from NMR titration and reduced viscosity experiment. ^{1}H NMR spectra of complex **1** showed a substantial downfield shift for pyrazole and pyridine ring proton and broadening of the peaks compared to ***L1*** due to complex **1** formation. Furthermore, the spectrum of **1** showed a clearly distinguishable three new low intensity peaks (8.74, 8.17, and 8.0 ppm) corresponding to pyridine and pyrazole protons of the metal free end group of the polymer chain. Interestingly, the phenyl peak of the ligand did not shift much even after metal coordination (Figures S3 and S4, Supporting Information). The integration ratio of the end group signal to the polymer **1** signal is 1:8, respectively (Figure 2).

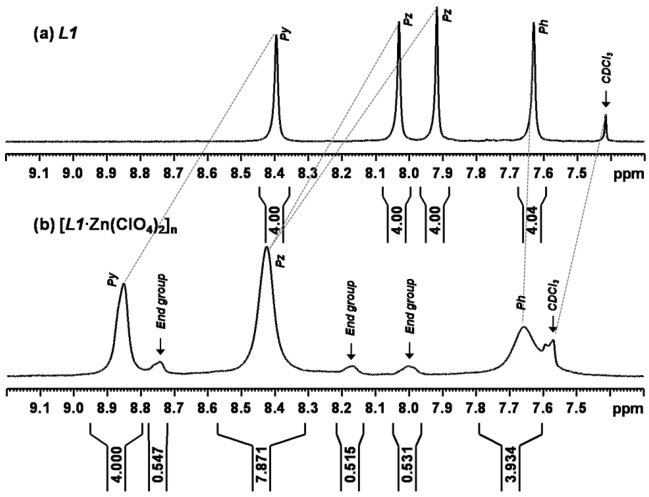

Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$-d_1/CD_3OD-d_4 (3:2)) spectra[16] of (a) ***L1*** and (b) polymer $[L1{\cdot}Zn(ClO_4)_2]_n$. TMS is used as a standard.

From the end group analysis the estimated molecular weight (M_n) of the highly soluble polymer **1** is ca. 9600 g/mol.

Taking advantage of the good solubility of MSP **1** in most of the organic solvents, by following "top-down approach" fabrication of a periodic microstripes composed of **1** was envisioned using microinject molding in capillaries (MIMIC) technique.[15] At first elastomeric stamp was fabricated by replica molding of polydimethylsiloxane (PDMS) on a commercially available compact disk.[9e]

The PDMS stamp was placed on a clean SiO_2 substrate. A 60 μL portion of dichloromethane solution containing MSP **1** (2 mg of **1** in 1 mL DCM) was dropped at one edge of the stamp so that the microchannels could be filled spontaneously by capillary action. After 30 min, the PDMS mold was carefully

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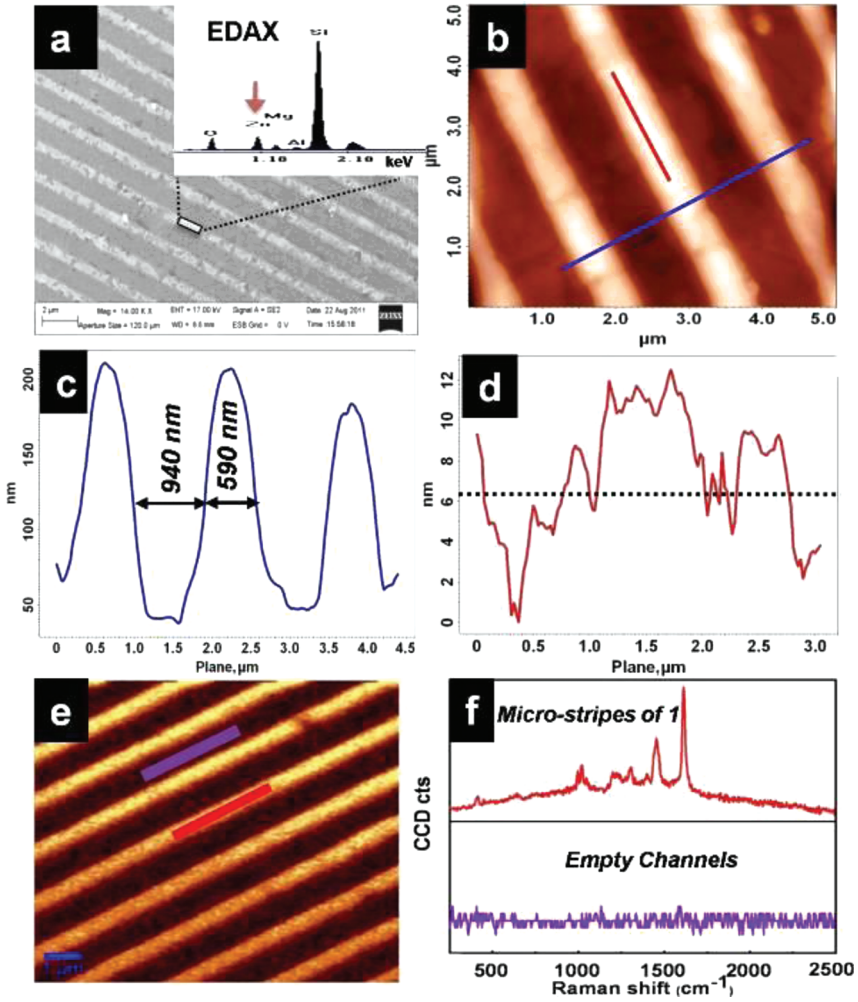

Figure 3. (a) FESEM image of microstripes of MSP **1** formed on silica substrate (scale bar is 2 μm). Inset shows the EDAX spectra of Zn-containing microstripes. (b) AFM topography image. (c) AFM height, width, and channel profiles of stripes shown in (b) as blue line. (d) Roughness profile of the microstripes shown in (b) as brown line. (e) Raman image of the microstripes (scale bar is 1 μm). (f) Raman spectra of microstripes and empty channels shown in (e) as red and blue lines, respectively.

peeled off to get periodic microstrips of several micrometers in length composed of coordination polymer **1** on a glass substrate. FESEM investigation of the sample revealed the formation of periodic microstrips several millimeters long which are well separated by empty channels (Figure 3a). AFM topography measurement of the same sample showed that the microstripes' width × height × roughness profiles are ca. 590 nm × ca. 200 nm × ~6 nm, respectively, with a uniform periodicity (Figure 3b–d). The empty channel width between the two adjacent microstrips is ca. 940 nm. Raman imaging/spectroscopy (633 nm laser) further confirmed that the microstripes were indeed composed of $[\boldsymbol{L1}\cdot Zn(ClO_4)_2]_n$ having uniform periodicity by exhibiting clear Raman shifts at 1613, 1454, 1398, 1307, 1201, 1020, 998, and 412 cm^{-1} from the microstripes (Figure 3e and f; red bar and lines) corresponding to the bulk of **1** (Figure S5, Supporting Information) and no Raman shift from the empty channels.

We presented an efficient 10-step synthetic protocol for the preparation of a series of novel back-to-back coupled tetraoctylated-bpp molecules ***L0–L3***. In addition, we demonstrated the preparation of solution processable metallosupramolecular coordination polymer from a representative ligand and its use in the fabrication ordered 1D microstripes using microinject molding technique. This general methodology can be applied to prepare soluble functional coordination polymers with diverse metal centers and their corresponding nano/micro structures. Fabrication of spin crossover nano/microstripes based on Fe(II) coordination polymer is in progress.

EXPERIMENTAL SECTION

2,2′,6,6′-Tetrakis(4-octyl-1*H*-pyrazol-1-yl)-4,4′-bipyridine (*L0*). In a 100 mL flask were taken DMSO (20 mL), compound **8** (100 mg, 0.178 mmol), bispinacolatodiborane (49 mg, 0.192 mmol), K_2CO_3 (80.48 mg, 0.582 mmol), and $Pd(PPh_3)_4$ (14.0 mg, 7 mol %). The flask containing the mixture was stirred at 80 °C under N_2 atmosphere for 18 h until the starting material **8** completely disappeared as monitored by TLC (eluent: EtOAc/hexane 5:95 ratio; R_f ~0.2). After the reaction mixture was cooled to room temperature, the solid was removed by filtration followed by washing with $CHCl_3$. The filtrate was then washed with deionized water (50 mL each) five times. The organic layer was dried over Na_2SO_4, and the concentrated organic fraction was subsequently purified by column chromatography (eluent: EtOAc/hexane 5:95 ratio) on silica gel to get an analytically pure white color powder of ***L0***: yield 55 mg (72%); mp 52–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.37 (s, 4H), 8.17 (s, 4H), 7.62 (s, 4H), 2.59–2.56 (t, 8H), 1.66–1.63 (m, 8H),

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1.37−1.26 (m, 40H), 0.91−0.88 (q, 12H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 151.0, 142.8, 124.9, 124.7, 108.5, 106.6, 31.9, 30.7, 29.4, 29.34, 29.3, 24.3, 22.7, 14.1; FTIR (KBr disk; ν in cm^{-1}) 2926, 2854, 1732, 1606, 1556, 1464, 1394, 1261, 1221, 1097, 1016, 970, 949, 862, 802, 725, 659, 611, 524; ESI MS m/z calcd 868.66, found 891.63 [M$^+$ + Na]. Anal. Calcd for $C_{54}H_{80}N_{10}$: C, 74.61; H, 9.28; N, 16.11. Found: C, 74.48; H, 9.21; N, 16.25.

1,4-Bis(2,6-bis(4-octyl-1*H*-pyrazol-1-yl)pyridin-4-yl)benzene (*L1*). Compound **8** (60 mg, 0.106 mmol), 1,4-phenylenediboronic acid (8.85 mg, 0.053 mmol), and $Pd(PPh_3)_4$ (6.17 mg, 5 mol %) were suspended in a N_2 gas bubbled solution of dioxane (20 mL) and 2 M Na_2CO_3 (5 mL). The mixture was heated to 80 °C for 3 d under nitrogen atmosphere. The mixture of solvents was removed in vacuo, and the remaining brown residue was treated with water and extracted with CH_2Cl_2 solvent. The separated organic layer was dried over Na_2SO_4, and the solvent was removed by evaporation. The solid residue was washed with MeOH (3 × 5 mL) to remove colored impurities and to get a white flakelike compound ***L1***: yield 45 mg (90%); mp 105−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.39 (s, 4H), 8.08 (s, 4H), 7.94 (S, 4H), 7.64 (s, 4H), 2.60−2.56 (t, 8H), 1.67−1.61 (t, 8H), 1.37−1.26 (m, 40H), 0.89−0.88 (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 152.8, 150.8, 142.6, 138.7, 127.8, 125.0, 124.5, 106.3, 31.9, 30.8, 29.5, 29.4, 29.3, 24.3, 22.7, 14.1; FTIR (KBr disk; ν in cm^{-1}) 3115, 2926, 2852, 1701, 1608, 1558, 1541, 1458, 1394, 1261, 1195, 1016, 954, 798; ESI-MS m/z calcd 944.69, found 967.66 [M$^+$ + Na]. Anal. Calcd for $C_{60}H_{84}N_{10}$: C, 76.23; H, 8.96; N, 14.82. Found: C, 76.12; H, 8.91; N, 14.75.

L2 and ***L3*** were prepared as per the above-mentioned procedure for ***L1*** using the corresponding diboronic acids **13** and **14**, respectively. Yield and spectral data are given below.

For ***L2***. Compound **8** (90 mg, 0.16 mmol), 1,4-phenylenediboronic acid (19.3 mg, 0.080 mmol) and $Pd(PPh_3)_4$ (9.26 mg, 5 mol %): yield 70 mg (86%); mp 158−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.39 (s, 4H), 8.11 (s, 4H), 7.95−7.93 (d, 4H), 7.81−7.79 (d, 4 H), 7.64 (s, 4H) 2.61−2.57 (t, 8H), 1.67−1.64 (t, 8H), 1.37−1.26 (m, 40H), 0.89−0.88 (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 153.2, 150.8, 142.6, 141.43, 137.0, 127.8, 127.7, 125.0, 124.4, 106.3, 31.9, 30.8, 29.4, 29.32, 29.27, 24.3, 22.7, 14.1; FTIR (KBr disk; ν in cm^{-1}): 2924, 2851, 1612, 1576, 1549, 1462, 1395, 1262, 1198, 1098, 1019, 804; ESI MS m/z calcd 1020.72, found 1043.68 [M$^+$ + Na]. Anal. Calcd for $C_{66}H_{88}N_{10}$: C, 77.60; H, 8.68; N, 13.71. Found: C, 77.85; H, 8.61; N, 13.61.

For ***L3***. Compound **8** (100 mg, 0.17 mmol), 1,4″-phenylenediboronic acid (28.3 mg, 0.089 mmol), and $Pd(PPh_3)_4$ (10.2 mg, 5 mol %): yield 68.4 mg (70%); mp 177−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.41 (s, 4H), 8.12 (s, 4H), 7.79−7.93 (d, 4H), 7.81−7.78 (d, 8H), 7.65−7.64 (d, 4 H),) 2.62−2.58 (t, 8H), 1.73−1.65 (t, 8H), 1.42−1.27 (m, 40 H), 0.93−0.90 (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 153.3, 150.8, 142.5, 139.6, 137.9, 136.6, 127.7, 127.6, 127.5, 125.1, 124.4, 106.23, 31.9, 30.8, 29.4, 29.34, 29.31, 24.3, 22.7, 14.1; FTIR (KBr disk; ν in cm^{-1}) 3437, 3354, 3242, 2957, 2920, 2851, 2521, 1798, 1659, 1576, 1481, 1393, 1323, 1190, 984, 920, 872, 808, 714, 633.

Preparation of Metallo Supramolecular Polymer [*L1*·Zn(ClO$_4$)$_2$]$_n$ (1). To a solution of ***L1*** (17.3 mg, 0.0183 mmol) in 20 mL of $CHCl_3$ was added 10 mL of a MeOH solution of $Zn(ClO_4)_2{\cdot}6H_2O$ (6.81 mg, 0.0182 mmol), and the solution was stirred for 30 min at room temperature. The obtained solution was concentrated in vacuo, and the yellowish-white polymer product **1** was precipitated by adding excess of hexane: yield 18.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$-d_1/CD_3OD-d_4 (3:2), 298 K) δ 8.85(s, 8H), 8.74 (s, 1H, end group), 8.42 (s, 16H), 8.17 (s, 1H, end group), 8.0 (s,1H, end group), 7.66 (s, 8H), 2.59 (s, 16H), 1.67 (s, 16H), 1.28 (m, 80H), 0.87(m, 24H); FTIR (KBr disk; ν in cm^{-1}) 3111, 2923, 2853, 1658, 1619, 1564, 1495, 1465, 1396, 1262, 1091(perchlorate Cl−O), 1012, 990, 970, 955, 930, 864, 831, 813, 795, 722, 622, 602; Raman (633 nm; ν in cm^{-1}) 1613, 1454, 1398, 1307, 1201, 1020, 998, and 412 cm^{-1}.

Ethyl 2,6-Bis(4-(oct-1-ynyl)-1*H*-pyrazol-1-yl)isonicotinate (4). A Schlenk tube was charged with ethyl 2′,6′-bis(4,4″-iodopyrazol-1,1″-yl)-isonicotinate **3** (2.6 g, 4.86 mmol) together with $Pd(PPh_3)_2Cl_2$ (170 mg, 0.242 mmol), triphenylphosphine (200 mg, 0.762 mmol), and CuI (200 mg, 1.05 mmol) as additional catalyst. Freshly distilled anhydrous triethylamine (20 mL) and 1,4-dioxane (10 mL) were added. The Schlenk tube was carefully degassed by freeze and thaw cycles. 1-Octyne (2.15 mL (d = 0.746 g/mL), 14.5 mmol) was added under argon by syringe, and the resulting mixture was heated to 80 °C for 48 h. It was then cooled to room temperature and allowed to stir for an additional 1 h. The mixture was filtered through filter paper and washed with 1,4-dioxane, and the filtrate was evaporated in vacuo to get a dark brown solid which was column chromatographed on silica (100−200 mesh) using (8:92) EtOAc/hexane to isolate **4** as a white solid: yield 2.0 g (82%); mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.56 (s, 2H), 8.34 (s, 2H), 7.78 (s, 2H), 4.48−4.43 (q, 2H), 2.43−2.39 (t, 4H), 1.65−1.58 (p, 5H), 1.5−1.4 (p, 7H), 1.34−1.25 (m, 10H), 0.94−0.91 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 163.8, 150.2, 145.0, 143.7, 129.1, 109.4, 107.0, 93.1, 70.4, 62.3, 31.4, 29.7, 28.7, 22.6, 19.5, 14.3, 14.1; FTIR (KBr disk; ν in cm^{-1}) 3113, 2928, 2856, 1730, 1618, 1574, 1469, 1390, 1348, 1305, 1234, 11890, 1099, 1030, 964, 895, 864, 819, 790, 769, 733, 655, 617, 507; LC−MS m/z calcd 499.29, found 500.50. Anal. Calcd for $C_{30}H_{37}N_5O_2$: C, 72.12; H, 7.46; N, 14.02. Found: C, 72.36; H, 7.41; N, 14.15.

Ethyl 2,6-Bis(4-octyl-1*H*-pyrazol-1-yl)isonicotinate (5). To a degassed solution of **4** (0.619 g, 1.23 mmol) in EtOAc (200 mL) was added 10% Pd/C (0.350 g, 0.3 mmol), and the mixture was stirred under a H_2 bladder and monitored by TLC. After 4 days, the mixture was filtered through a Celite plug to remove activated Pd/C. Afterward, the plug was washed with 100 mL of EtOAc and the collected fraction was concentrated in vacuo to afford **5** as yellowish gummy oil: yield 0.618 g (99%); ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.30 (s, 2H), 8.28 (s, 2H), 7.6 (s, 2H), 4.46−4.42 (q, 2H), 2.56−2.53 (t, 4H), 1.64−1.62 (t, 4H), 1.36−1.24 (m, 23H), 0.89−0.88 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 164.1, 150.8, 143.3, 142.9, 124.9, 124.8, 108.2, 62.0, 31.9, 30.6, 29.4, 29.35, 29.30, 24.30, 22.7, 14.25, 14.1; FTIR (KBr disk; ν in cm^{-1}) 2924, 2853, 1612, 1576, 1547, 1464, 1392, 1261, 1099, 1016, 804; LC−MS analysis m/z calcd 507.71, found 508.65. Anal. Calcd for $C_{30}H_{45}N_5O_2$: C, 70.97; H, 8.93; N, 13.79. Found: C, 70.79; H, 8.86; N, 13.65.

2,6-Bis(4-(oct-1-ynyl)-1*H*-pyrazol-1-yl)isonicotinic Acid (6). Compound **5** (0.6 g, 1.18 mmol) was dissolved in 25 mL of THF. Aqueous LiOH (0.2 g, 8.33 mmol, 7 equiv in 75 mL of water) was added to the THF solution. After 1 h, the THF was removed in vacuo, and the solution was cooled in an ice bath. To this was then slowly added 27 mL of 2 M HCl. After 1 h, the white solid product **6** was isolated by filtration followed by drying in air (0.5 g, >98%): mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.46 (s, 2H), 8.36 (s, 2H), 7.72 (s, 2H), 4.8−4.6 (broad, OH) 2.60−2.56 (t, 4H), 1.69−1.63 (t, 4H), 1.38−1.24 (m, 20H), 0.92−0.89 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 165.8, 150.6, 143.6, 143.0, 125.3, 124.9, 109.0, 31.9, 30.6, 29.4, 29.4, 24.3, 22.7, 14.1; FTIR (KBr disk; ν in cm^{-1}) 3427 (broad-COOH), 3113, 2926, 2854, 1707, 1618, 1574, 1460, 1392, 1261, 1192, 1060, 964, 802, 721, 673, 611, 408; LC−MS analysis m/z calcd 479.65, found 478.40.

2,6-Bis(4-octyl-1*H*-pyrazol-1-yl)pyridin-4-amine (7). Compound **6** (0.4 g, 0.83 mmol, 1 equiv) was dissolved in a mixture of 3:1 CH_2Cl_2/THF (50 mL). To this was slowly added oxalyl chloride (0.09 mL, 1.017 mmol, 1.22 equiv) and the mixture stirred at room temperature. After 4 h, the solvent was removed in vacuo, and the resultant residue was dissolved in dry acetone (10 mL). This acetone mixture was added to a solution of NaN_3 (0.234 g, 3.60 mmol, 4.32 equiv) in H_2O (20 mL). The solution was immediately extracted with Et_2O (3 × 20 mL). The combined organic fraction was dried with $MgSO_4$ and concentrated to yield a white solid. The solid was redissolved in 50 mL of dry benzene; trifluoroacetic acid was added (0.09 mL, 1.25 mmol, 1.50 equiv), and the solution was heated to reflux for 16 h. After cooling, the benzene was removed in vacuo, and the residue was redissolved in CH_3OH (50 mL). Solid K_2CO_3 was added (0.250 g, 1.80 mmol, and 2.17 equiv) and the mixture vigorously stirred for 8 h. After 95% of the CH_3OH was removed in vacuo, 70 mL of H_2O was added, and the mixture was cooled in an ice bath for 2 h. The resulting precipitate was isolated by filtration

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followed by drying in air (0.307 mg, 78%): mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.29 (s, 2H), 7.53 (s, 2H), 7.03 (s, 2H), 4.51 (s, 2H), 2.55−2.51 (t, 4H), 1.65−1.61 (m, 4H), 1.34−1.26 (m, 20H), 0.90−0.87 (q, 6H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 156.8, 151.2, 141.9, 125.0, 123.8, 94.1, 31.9, 30.8, 29.4, 29.3, 29.28, 24.3, 22.7, 14.1; FTIR (KBr disk; ν in cm^{-1}) 3437, 3354, 3238, 2920, 2851, 1655, 1575, 1479, 1394, 1190, 983, 920, 871, 808, 713, 632, 459; LC−MS analysis m/z calcd 450.34, found 451.55. Anal. Calcd for $C_{27}H_{42}N_6$: C, 71.96; H, 9.39; N, 18.65. Found: C, 72.13; H, 9.31; N, 18.56.

4-Iodo-2,6-bis(4-octyl-1*H*-pyrazol-1-yl)pyridine (8). Compound **7** (0.5 g, 1.108 mmol), iodine (0.562 g, 2.217 mmol), and KI (0.552 g, 3.325 mmol) were suspended in degassed solutions of dichloromethane/isoamyl nitrite (2:1, 30 mL). The mixture was heated with stirring for 12 h under N_2 atmosphere. After cooling, the mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ (100 mL) and extracted with dichloromethane (3 × 30 mL). The collected orange organic layers were dried over Na_2SO_4, and the solvent was evaporated in vacuo. The crude orange product was purified by column chromatography on silica using a mixture of *n*-hexane/CH_2Cl_2 (3:2) to afford a white color product **8** (210 mg, 34%): mp 75−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.25 (s, 2H), 8.15 (s, 2H), 7.57 (s, 2H), 2.54−2.50 (t, 4H), 1.65−1.58 (m, 4H), 1.33−1.27 (m, 20H), 0.89−0.86 (q, 6H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 149.8, 143.0, 124.9, 124.8, 117.5, 108.5, 31.9, 30.7, 29.4, 29.3, 24.2, 22.7, 14.1; FTIR (KBr disk; ν in cm^{-1}) 3103, 2926, 2851, 1734, 1585, 1568, 1454, 1392, 1263, 1190, 1157, 1053, 1018, 960, 866, 839, 802, 760, 706, 646, 609, 540; LC−MS analysis: m/z calcd 562.0, found 561.23. Anal. Calcd for $C_{27}H_{40}IN_5$: C, 57.75; H, 7.18; N, 12.47. Found: C, 57.68; H, 7.25; N, 12.36.

2,6-Bis(4-(oct-1-ynyl)-1*H*-pyrazol-1-yl)isonicotinic Acid (9). Compound **4** (0.6 g, 1.18 mmol) was dissolved in 25 mL of THF, and 75 mL of aqueous LiOH (0.2 g, 8.33 mmol, 7 equiv) was added. After 1 h, the THF was removed in vacuo and the solution was cooled in an ice bath. Subsequently, 2 M HCl (27 mL) was slowly added. After 1 h, the white solid was isolated by filtration and air-dried to get compound **9** (0.5 g, 90%): ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ: 8.55 (s, 2H), 8.40 (s, 2H), 7.81 (s, 2H), 2.42 (s, 4H), 1.62 (s, 4H),1.46 (s, 4H), 1.35 (s, 8H), 0.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 166.9, 150.2, 145.1 143.0, 129.2, 109.8, 107.2, 93.2, 70.3, 31.4, 28.7, 22.6, 19.5, 14.1; FTIR (KBr disk; ν in cm^{-1}) 2924, 2853, 1701, 1618, 1572, 1460, 1348, 1306, 1258, 1182, 1030, 962, 891, 816, 795, 773, 703, 665, 534. Anal. Calcd for $C_{28}H_{33}N_5O_2$: C, 71.31; H, 7.05; N, 14.85. Found: C, 71.19; H, 7.12; N, 14.68.

1,1′-(1,1′-(4-Aminopyridine-2,6-diyl)bis(1*H*-pyrazole-4,1-diyl))dioctan-1-one (10). Compound **9** (0.4 g, 0.83 mmol, 1 equiv) was dissolved in a mixture of 3:1 CH_2Cl_2/THF (50 mL). To this was slowly added oxalyl chloride (0.09 mL, 1.017 mmol, 1.22 equiv) at room temperature. After 4 h, the solvent was removed in vacuo, and the residue was dissolved in dry acetone (10 mL). This was added to a solution of NaN_3 (0.234 g, 3.60 mmol, 4.32 equiv) in H_2O (20 mL). The solution was immediately extracted with Et_2O (3 × 20 mL). The organic fractions were combined, dried with $MgSO_4$, and concentrated to give a white solid. The solid was redissolved in 50 mL of dry benzene; trifluoroacetic acid was added (0.09 mL, 1.25 mmol, 1.50 equiv), and the solution was heated to reflux for 16 h. After cooling, the benzene was removed in vacuo, and the resultant residue was dissolved in CH_3OH (50 mL). To this was added K_2CO_3 (0.250 g, 1.80 mmol, and 2.17 equiv) and the mixture vigorously stirred. After 8 h, 95 vol % of the CH_3OH was removed on a rotary evaporator, 70 mL of H_2O was added, and the mixture was cooled in an ice bath for 2 h. The resulting white precipitate (**10**) was isolated by filtration (0.37 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.95 (s, 2H), 8.08 (s, 2H), 7.18 (s, 2H), 4.84 (s, 2H), 2.86 (s, 4H), 1.75−1.73 (m, 4H), 1.29−1.25 (m, 15H), 0.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 195.2, 157.3, 150.5, 142.0, 129.1, 125.1, 96.3, 40.7, 31.7, 29.6, 29.3, 29.2, 24.3, 22.6, 14.1; FTIR (KBr disk; ν in cm^{-1}) 3466, 3434, 3364, 3229, 3113, 2926, 2855, 1670, 1632, 1547, 1487, 1410, 1186, 982, 943, 941, 835, 788, 723, 642, 540; LC−MS analysis m/z calcd 478.31, found 479.65 (positive mode). Anal. Calcd for $C_{27}H_{38}N_6O_2$: C, 67.75; H, 8.00; N, 17.56. Found: C, 67.86; H, 8.09; N, 17.45.

1,1′-(1,1′-(4-Iodopyridine-2,6-diyl)bis(1*H*-pyrazole-4,1-diyl))dioctan-1-one (11). 1,1′-(1,1′-(4-Aminopyridine-2,6-diyl)bis(1*H*-pyrazole-4,1-diyl))dioctan-1-one (**10**) (0.5 g, 1.04 mmol), iodine (0.562 g, 2.217 mmol), and KI (0.552 g, 3.325 mmol) were suspended in a degassed mixture of dichloromethane/isoamyl nitrite (2:1, 30 mL) and heated with stirring for 12 h. After cooling, the mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ (100 mL) and extracted with dichloromethane (3 × 30 mL). The collected orange organic layer was dried over Na_2SO_4, and the solvent was evaporated in vacuo. The crude orange product was purified by column chromatography on silica using a mixture of *n*-hexane/CH_2Cl_2 (3:2) to afford a white product of **11** (230 mg, 38%): mp 154−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 8.95 (s, 2H), 8.35 (s, 2H), 8.13 (s, 2H), 2.88−2.85 (t, 4H), 1.77−1.71 (t, 4H), 1.39−1.35 (m, 12H), 0.87−0.86 (t, 6H); ^{13}C NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 194.9, 149.2, 142.8, 129.1, 125.9, 120.4, 109.5, 40.9, 31.7, 29.3, 29.2, 24.2, 22.6, 14.1; FT-IR (KBr) ν in cm^{-1} 3111, 2926, 2851, 1663, 1595, 1549, 1456, 1414, 1269, 1190, 1130, 962, 851, 793, 768, 663, 623, 540. Anal. Calcd for $C_{27}H_{36}IN_5O_2$: C, 55.01; H, 6.16; N, 11.88; Found: C, 55.16; H, 6.21; N, 11.68.

1,1′,1′′,1′′′-(1,1′,1′′,1′′′-(4,4′-(1,4-Phenylene)bis(pyridine-6,4,2-triyl))tetrakis(1*H*-pyrazole-4,1-diyl))tetraoctan-1-one (12). Compound **11** (76 mg, 0.131 mmol), 1,4-phenylenediboronic acid (10.8 mg, 0.655 mmol), and $Pd(PPh_3)_4$ (7.9 mg, 0.0068 mmol, 5 mol %) were suspended in a degassed mixed solution of 1,4-dioxane (20 mL) and 2 M Na_2CO_3 (5 mL) and heated to 80 °C for 3 d under nitrogen atmosphere. The mixtures of solvents were removed by in vacuo, and the remaining residue was treated with water and extracted with CH_2Cl_2 solvent. The separated organic layer was dried over Na_2SO_4, and the solvent was removed by evaporation. The solid residue was washed with MeOH (3 × 5 mL) to obtain white compound **12**: yield 30 mg (46%); mp 282−283 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 9.08 (s, 4H), 8.26−8.20 (d, 8H), 7.97 (s, 4H), 2.92 (s, 8H), 1.80 (s, 8H), 1.40−1.26 (m, 32H), 0.91 (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$-d_1, 298 K) δ 195.0, 153.6, 150.2, 142.5, 129.1, 128.2, 127.9, 125.7, 109.0, 40.9, 31.7, 29.3, 29.2, 24.2, 22.6, 14.1; FTIR (KBr disk; ν in cm^{-1}) 2926, 2853, 1674, 1615, 1545, 1472, 1408, 1202, 1150, 959, 831, 795, 664. Anal. Calcd for $C_{60}H_{76}N_{10}O_4$: C, 71.97; H, 7.65; N, 13.99. Found: C, 71.76; H, 7.61; N, 13.85.

4,4′-Diiodobiphenyl (15). Compound **15** was synthesized according to the reported literature procedure[12] in 95% yield: ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 7.82−7.80 (d, 4H), 7.47−7.45 (d, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ 139.0, 138.2, 129.2, 94.8; LC−MS analysis calcd m/z calcd 406.0, found 405.65; FTIR (KBr disk; ν in cm^{-1}): 3059, 2926, 2857, 1647, 1578, 1470, 1379, 1126, 1065, 993, 802, 459. Anal. Calcd for $C_{12}H_8I_2$: C, 35.50; H, 1.99. Found: C, 35.41; H, 1.92.

***p*-Diphenyldiboronic Acid (13).** At −78 °C, *n*-butyllithium (6 mL, 1.6 M in hexane) was added dropwise to a solution of 4,4′-diiodobiphenyl **15** (1.0 g; 2.07 mmol) in dry THF (20 mL). The resultant yellowish suspension was then stirred for an additional 1 h at −78 °C. Trimethyl borate (1.5 mL; 12.42 mmol) was added within 15 min at −30 °C. The resultant pale yellowish solution was stirred for 15 h at room temperature. The reaction mixture was acidified with 2 M HCl (50 mL) to get an insoluble white precipitate of **14**: yield 0.55 g (82%); ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 8.09 (s, 4H), 7.89−7.87 (d, 4H), 7.67−7.65 (d, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ 142.0, 135.3, 133.8 (low intensity due to quadruple resonance between ^{11}B and ^{13}C nucleus), 126.1; FTIR (KBr disk; ν in cm^{-1}) 3370 (broad, −OH), 1607, 1555, 1535, 1379, 1341, 1155, 1092, 1022, 999, 814, 737, 627.

***p*-Terphenyl (16).** *p*-Dibromobenzene (2 g, 8.47 mmol), phenylboronic acid (2.27 g, 18.64 mmol), and $Pd(PPh_3)_4$ (0.489 g, 0.423 mmol) were discharged in a degassed 1,4-dioxane (20 mL), and 5 mL of 2 M Na_2CO_3 was added to this mixture. Then the reaction mixture was heated at 70 °C for 3 days under inert atmosphere. The progress of the reaction was monitored by TLC. After the disappearance of starting material, the reaction mixture cooled to room temperature and

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dried in vacuo. Then the residue was treated with water and extracted with DCM. The organic layer was collected and dried over sodium sulfate. The solvent was dried in vacuo, and the resultant solid residue was washed with petroleum ether to remove colored impurities and to obtain compound **15** in pure form: yield 1.4 g (72%); ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 7.7 (s, 4H), 7.67−7.65 (d, 4H), 7.5−7.46 (t, 4H), 7.4−7.36 (t, 2H); LC−MS analysis calcd m/z 230.30, found 231.1; FTIR (KBr disk; ν in cm^{-1}) 2926, 1734, 1651, 1618, 1559, 1541, 1472, 1234, 1182, 1107, 1024, 837, 746, 687, 540, 457. Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.76; H, 6.21.

Diiodoterphenyl (17). Compound **17** was synthesized according to the literature procedure:[12] yield (81%); ^{1}H NMR (400 MHz, $CDCl_3$-d_1, 298 K) δ 7.84−7.82 (d, 4H), 7.76 (s, 4H), 7.55−7.53 (d, 4H); FTIR (KBr disk; ν in cm^{-1}) 2917, 1559, 1456, 1393, 802, 461. Anal. Calcd for $C_{18}H_{12}I_2$: C, 44.84; H, 2.51. Found: C, 44.75; H, 2.58.

***p*-Terphenyldiboronic Acid (14).** At −78 °C, *n*-butyllithium (6 mL; 1.6 M in hexane) was added dropwise to a solution of diiodo-*p*-terphenyl **17** (1.0 g; 2.07 mmol) in dry THF (20 mL). The resultant yellowish suspension was then stirred for an additional 1 h at −78 °C. The solution was slowly warmed to −30 °C, and trimethyl borate (1.5 mL; 12.42 mmol) was added dropwise within 15 min. The resultant pale yellowish solution was stirred for 15 h at room temperature. The reaction mixture was acidified with 2 M HCl (50 mL), and the insoluble precipitate was filtered and air-dried to get **17** as a white solid: yield 0.55 g (82%); ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 8.07 (s, 4H), 7.90−7.88 (d, 4H), 7.79 (s, 4H), 7.71−7.69 (d, 4H).^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ 141.4, 139.7, 135.3, 134.8 (low intensity due to quadruple resonance between ^{11}B and ^{13}C nucleus), 127.7, 126.0; FTIR (KBr disk; ν in cm^{-1}) 3370 (broad, −OH), 1607, 1555, 1535, 1379, 1341, 1155, 1092, 1022, 999, 814, 737, 627.

■ ASSOCIATED CONTENT

Supporting Information

General experimental methods, characterization details, fluorescent anisotrophy, reduced viscosity, and NMR titration data of ***L1*** with Zn(II). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rcsc@uohyd.ernet.in, chandrasekar100@yahoo.com.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995. (b) Schubert, U. S.; Hofmeier, H.; Newkome, G. R. *Modern Terpyridine Chemsitry*; Wiley-VCH: Weinheim, 2006; p 69. (c) Constable, E. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1405. (d) Collin, J. P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434. (e) Chelucci, G; Thummel, R. P. *Chem. Rev.* **2002**, *102*, 3129. (f) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246. (g) Whittell, G. R.; Hager, M. D.; Schubert, U. S.; Manners, I. *Nat. Mater.* **2011**, *10*, 176.

(2) (a) Burnworth, M.; Tang, L.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. *Nature* **2011**, *472*, 334. (b) Iyer, P. K.; Beck, J. B.; Weder, C.; Rowan, S. J. *Chem. Commun.* **2005**, 319.

(3) (a) Mas-Balleste, R.; Gomez-Herrero, J.; Zamora, F. *Chem. Soc. Rev.* **2010**, *39*, 4220. (b) Kelch, S.; Rehahn, M. *Macromolecules* **1998**, *31*, 4102.

(4) (a) Dobrawa, R.; Lysetska, M.; Ballester, P.; Grune, M.; Würthner, F. *Macromolecules* **2005**, *38*, 1315. (b) Stepanenko, V.; Stocker, M.; Muller, P.; Buchner, M.; Wurthner, F. *J. Mater. Chem.* **2009**, *19*, 6816. (c) Bernhard, S.; Goldsmith, J. I.; Takada, K.; Abruña, H. D. *Inorg. Chem.* **2003**, *42*, 4389. (d) Yu, S.-C.; Kwok, C.-C.; Chan, W.-K.; Che, C.-M. *Adv. Mater.* **2003**, *15*, 1643. (e) Kadjane, P.; Starck, M.; Camerel, F.; Hill, D.; Hildebrandt, N.; Ziessel, R.; Charbonnière, L. J. *Inorg. Chem.* **2009**, *48*, 4601.

(5) (a) Schwarz, G.; Bodenthin, Y.; Geue, T.; Koetz, J.; Kurth, D. G. *Macromolecules* **2010**, *43*, 494. (b) Miyashitaa, N.; Kurth, D. G. *J. Mater. Chem.* **2008**, *18*, 2636.

(6) (a) Mugemana, C.; Guillet, P.; Hoeppener, S.; Schubert, U. S.; Fustin, C. A.; Gohy, J. F. *Chem. Commun.* **2010**, *46*, 1296. (b) Hager, M. D.; Greil, P.; Leyens, C.; Zwaag, S. V. D.; Schubert, U. S. *Adv. Mater.* **2010**, *22*, 5424. (c) Ruben, M.; Landa, A.; Lörtscher, E.; Riel, H.; Mayor, M.; Görls, H.; Weber, H. B.; Arnold, A.; Evers, F. *Small* **2008**, *4*, 2229.

(7) (a) Li, Y.; Huffmana, J. C.; Flood, A. H. *Chem. Commun.* **2007**, 2692. (b) Meudtner, R. M.; Ostermeier, M.; Goddard, R.; Limberg, C.; Hecht, S. *Chem.—Eur. J.* **2007**, *13*, 9834. (c) Li, Y.; Flood, A. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 2649−2652. (d) Meudtner, R. M.; Hecht, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4926. (e) Juwarker, H.; Lenhardt, J. M.; Pham, D. M.; Craig, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 3740.

(8) (a) Chandrasekhar, N.; Chandrasekar, R. *J. Org. Chem.* **2010**, *75*, 4852. (b) Chandrasekhar, N.; Chandrasekar, R. *Angew. Chem., Int. Ed.* **2012**, DOI: 10.1002/anie.201106652.

(9) (a) Rajadurai, C.; Fuhr, O.; Kruk, R.; Ghafari, M.; Hahn, H.; Ruben, M. *Chem. Commun.* **2007**, 2636. (b) Chandrasekar, R.; Schramm, F.; Fuhr, O.; Ruben, M. *Eur. J. Inorg. Chem.* **2008**, *17*, 2649. (c) Chandrasekhar, N.; Chandrasekar, R. *Chem. Commun.* **2010**, *46*, 2915. (d) Basak, S.; Chandrasekar., R. *Adv. Funct. Mater.* **2010**, *21*, 667. (e) Cavallini, M.; Bergenti, I.; Milita, S.; Ruani, G.; Salitros, I.; Qu, Z.-R.; Chandrasekar, R.; Ruben, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8596. (f) Zoppellaro, G.; Enkelmann, V.; Geies, A.; Baumgarten, M. *Org. Lett.* **2004**, *6*, 4929.

(10) (a) Basak, S.; Hui, P.; Chandrasekar, R. *Synthesis* **2009**, *23*, 4042. (b) Chandrasekhar, N.; Chandrasekar, R. *Dalton Trans.* **2010**, *39*, 9872.

(11) Amb, C. M.; Rasmussen, S. C. *J. Org. Chem.* **2006**, *71*, 4696.

(12) Schlickum, U.; Decker, R.; Klappenberger, F.; Zoppellaro, G.; Klyatskaya, S.; Auwärter, W.; Neppl, S.; Kern, K.; Brune, H.; Ruben, M.; Barth, J. V. *J. Am. Chem. Soc.* **2008**, *130*, 11778.

(13) Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 1020.

(14) Solanki, N. K.; Leech, M. A.; McInnes, E. J. L.; Mabbs, F. E.; Howard, J. A. K.; Kilner, C. A.; Rawson, J. M.; Halcrow., M. A. *J. Chem. Soc., Dalton Trans.* **2002**, 1295.

(15) Kim, E.; Xia, Y.; Whitesides, G. M. *Nature* **1995**, *376*, 581.

(16) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem. 62*, 7512.