Self-assembly molecular architectures with novel cyclic dimers

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Abstract

Highly emissive conjugated compounds containing pyridine (or pyrimidine) and cyano ligands have been synthesized by palladium-catalyzed cross-coupling reaction. These ligands readily react with $Re(CO)_3(THF)_2Br$ to form cyclic supramolecules by self-assembly processes. At room temperature these supramolecules are emissive, and the emission is ligand-localized, as evidenced from the Stokes shift and the lifetime data.
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1. Introduction

Metal-containing supramolecules and coordination polymers is an area of expanding development because these compounds not only provide useful models for molecular recognition and light harvesting but also have potential applications in materials science [1]. Self-assembly inorganic cyclophane molecules have emerged as an important class of supramolecules in the past decade [2]. Such macrocycles are attractive in sensing technology: (a) the cavity inside these molecules can trap some guest molecules and (b) the detection of the guest molecules is possible through the photoluminescence characteristics or changes in redoxpotential values of the host.

Macrocycles in which metals are all linked by conjugated spacers appear to be very interesting because molecular wire type spacers are expected to enhance the sensitivity of chemosensors, similar to conjugated polymer-based chemical sensors [3]. Such compound may also find applications in other aspects, such as: (a) third-order non-linear optical materials [4]; (b) electrochromic materials tunable through the redox of the metal center [5]; (c) sensing materials to detect molecules or ions [6].

We have been interested in metal-containing macrocycles in which metals are linked by conjugated spacers only. Transition metal complexes generally suffer from very low luminescent quantum yields due to the presence of heavy atom effects [7]. It was thought that use of strongly emissive spacers would partially compensate for this effect. The prerequisite for the construction of self-assembly metal-containing macrocycles is the availability of ditopic (or oligotopic) ligands [8], and oligo- and polypyridyl (cyano) ligands are probably the most widely used ligands for this purpose.

Here, we describe the preparation and characterization of a series of *fac*-tricarbonyl rhenium(I)-base self-assembly macrocyclic complexes with conjugated ligands containing pyridyl (pyrimidyl) and cyano moiety.

2. Results and discussion

The conjugated ligands **L1**–**L4** were conveniently prepared by a multi-step reaction. Palladium-catalyzed Sonogashira coupling [9] reaction with trimethylsilylacetylene and desilylation by KOH in methanol at room temperature led to the desired terminal acetylenes. These terminal

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acetylenes underwent facile cross-coupling reactions with 4-bromo-2-iodopyridine, 4-bromo-2-iodopyrimidine and 4-bromo-2-chloropyridine to provide the conjugated ligands **L1**–**L4** in good yields. All the ligands described here were thoroughly characterized by NMR, mass spectrometry, and elemental analysis. To facilitate ligand substitution reaction of **L1**–**L4** for CO in Re(CO)$_5$Br, Re(CO)$_5$Br was converted to Re(CO)$_3$(THF)$_2$Br by refluxing the THF solution of Re(CO)$_5$Br for one day under an N$_2$ atmosphere [10]. The conjugated ligands **L1**–**L3** readily reacted with Re(CO)$_3$(THF)$_2$Br in THF solvent to yield soluble molecular cyclic dimers **S1**, **S2** and **S3** with a rectangular geometry (Schemes 1 and 2). On the contrary, the reaction of **L4** with Re(CO)$_3$(THF)$_2$Br in THF solvent only leads to monomeric complex **S4** which contains two **L4** ligands (Scheme 3).

The growth of single crystals for **S1**–**S4** was not successful. However, the elemental analyses, mass spectra, the ^{1}H NMR, the infrared and the UV–Vis spectra of **S1**–**S4** (Tables 1 and 2) are consistent with their formulation. The isomer of **Sn** ($n = 1$–3), **Sn**′, with a triangular geometry as shown in Fig. 1, cannot be excluded [11]. Fig. 2 is the FABMS of **S3**. Though no parent peak was observed, the peaks attributed to $(M - CO)^+$ and $(M - Br)^+$ can be clearly identified (Fig. 2(a)). The relative isotope distribu-

tion of the $(M - CO)^+$ fragment fits well with the simulated spectra (Fig. 2(b)). Furthermore, the peaks due to higher oligomers are elusive. The FABMS of **S1** and **S2** are similar to those of **S3**. For **S4**, there was no fragment due to cyclic dimers analogous to **S1**–**S3**. Instead, only the parent peak attributed to the monomer was detected.

Infrared spectra in the carbonyl stretching region for **S1**–**S4** exhibit tricarbonyl stretching patterns between 1890 and 2024 cm^{-1} that are typical of *fac*-Re(LL)(CO)$_3$X complex [12]. One broad v(CN) peak with a prominent shoulder was observed in CH$_2$Cl$_2$. Coordination of the ligands renders the v(CN) values to be lower than those of the corresponding free ligands by ~20 cm^{-1}. As expected, α-pyridyl protons in these cyclic complexes **S1**, **S2** and **S3** shift downfield relative to their free ligands due to the dative bonding nature of the nitrogen (pyridyl or pyrimidyl) lone pair to the Re(I) center. On the contrary, the chemical shifts of the α-pyridyl protons of **S4** remain almost the same as those of **L4**. This observation further supports the monomeric nature of **S4**.

Table 2 summarizes the photophysical data of **L1**–**L4** and **S1**–**S4**. All the ligands possess intense π–π* absorption in the near-UV region. The metal complexes **S1**–**S3** possess two or three substantially overlapping ligand-localized π–π* and MLCT (metal to pyridyl or to pyrimidyl dπ → pπ*)
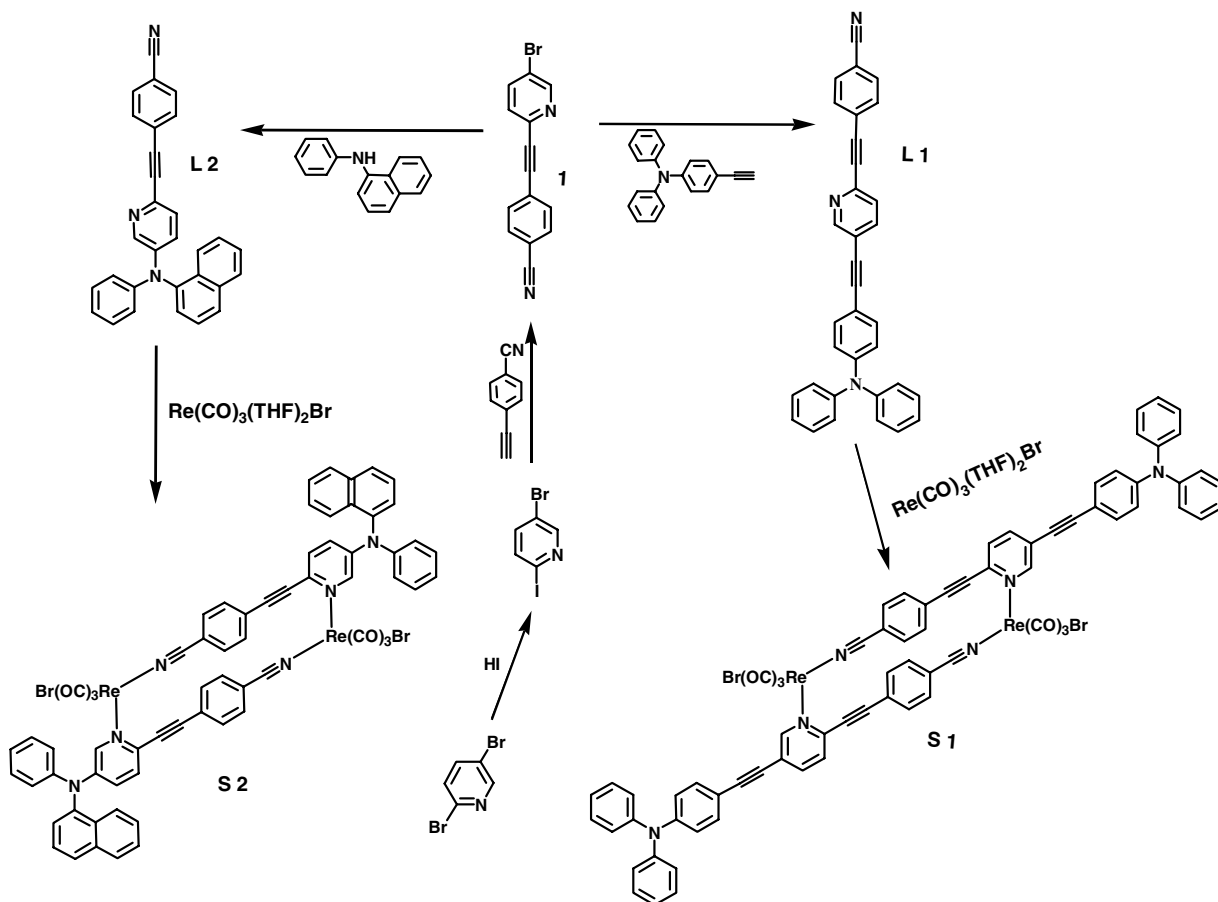
Scheme 1.

Scheme 2.

Scheme 3.
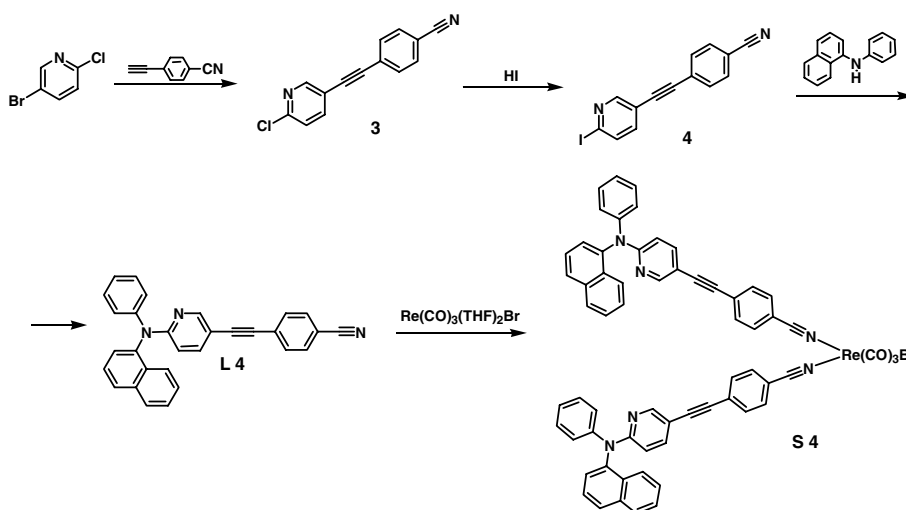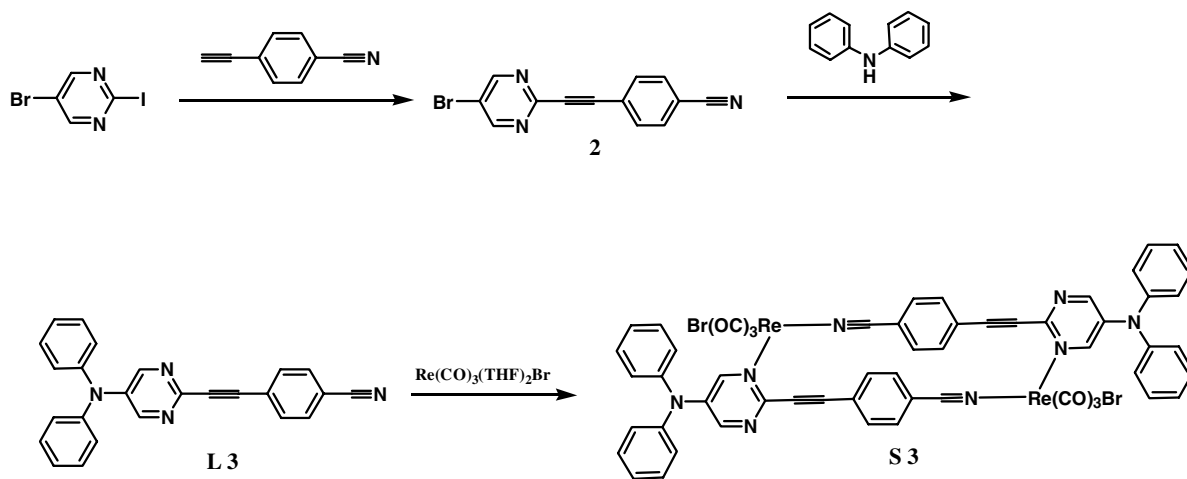
Table 1
Infrared CO and CN stretching frequency data for the compounds in CH₂Cl₂

Compound	v (CN, cm^{-1})	v (CO, cm^{-1})		
L1	2230 (w)	2023 (s)	1909 (m)	1891 (s)
S1	2208 (w)			
L2	2229 (w)	2026 (s)	1923 (m)	1906 (s)
S2	2210 (w)			
L3	2228 (w)	2024 (s)	1924 (m)	1890 (s)
S3	2209 (w)			
L4	2230 (w)	2024 (s)	1909 (m)	1892 (s)
S4	2213 (w)			

absorption bands, with the latter appearing at lower energy (see Fig. 3 for **L1** and **S1**). The monomeric complex, **S4**, has no MLCT bands due to the absence of Re–pyridine or pyrimidine linkage. At room temperature the complexes **S1**–**S4** exhibit wavelength-independent luminescence and a single-exponential decay profile with emission lifetime

ranging from 1.37 to 2.28 ns. The relatively small Stokes shift and the short lifetime indicate that the emission is mainly ligand-localized π–π^* fluorescence. The solution quantum yields of **S1**–**S4** are at least one order lower than those of their free ligands. This can be attributed to the large spin–orbit coupling exerted from Re(I) atoms [13], which led to intersystem crossing from the $^1\pi$–π^* state to the non-emissive ^{3}MLCT and/or $^3\pi$–π^* state [14].

Whether ligation of **L1**–**L3** to two rhenium centers to form **S1**–**S3** proceeds simultaneously or in a stepwise manner is not known at present. No monomeric analogues of **S4** can be detected if only 0.5 equivalent of **L1**–**L3** was used in the reaction. Though **L1** and **L4** are isomeric, only the former leads to the formation of the cyclic dimer. The geometrical constraint around the Re center with pyridine (or pyridimidine) linkage is expected to be very similar in **S1**–**S3**. However, the two pyridyl nitrogen atoms are farther away compared to those in **S1**–**S3**, and are not likely to span the *cis* coordination sites of the Re(CO)₃Br fragment.

Table 2
Electronic absorption and emission data for the compounds

Compound	Absorption spectra λ_{max} (nm)	Emission[a,b] λ_{em} (nm)	Quantum yield Φ_{em} (%)	Lifetime τ (ns)	k_r[c] (s)
L1	305, 327, 394	545	61	1.32	4.62×10^8
S1	303, 330, 480	564	0.1	1.61	6.21×10^5
L2	270, 377	496	52	1.65	3.15×10^8
S2	300 (sh), 403	513	0.3	2.28	1.32×10^6
L3	272, 376	513	50	2.13	2.35×10^8
S3	279 (sh), 429	517	0.1	1.97	5.08×10^5
L4	365	479	76	1.31	5.76×10^8
S4	367	497	3	1.35	2.22×10^7

[a] $\lambda_{ex} = 350$ nm.
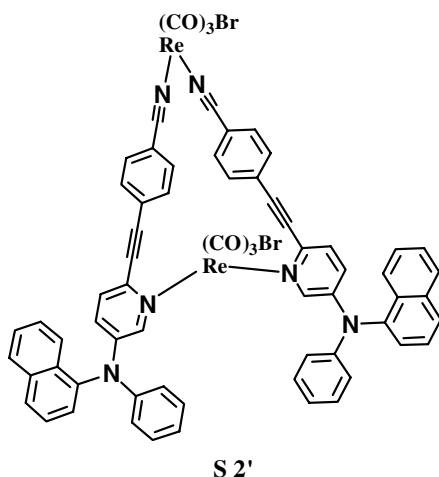[b] CH_2Cl_2 solution at room temperature.
[c] $k_r = \Phi/\tau$.

Fig. 1. The structural isomer of **S2**, **S2′**, with triangular geometry.

In conclusion, we have synthesized highly emissive conjugated ligands containing a pyridine or pyrimidine moiety as the central core, and cyano moiety as the end. These compounds are demonstrated to be useful building blocks for the construction of macrocyclic supramolecules with unprecendented geometries. Because of the luminescent nature of some of the complexes, sensing applications may be possible. Extension and further exploration of this study is in progress.

3. Experimental

3.1. General procedures

All reactions and manipulations were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed under N_2 with the use of silica gel (230–400 mesh, Macherey–Nagel GmbH & Co.) as the stationary phase in a column of 30 cm in length and 2.0 cm in diameter. 4-Ethynylbenzonitrile [15], 5-bromo-2-iodopyridine [16], (4-ethynylphenyl)diphenylamine [17], 5-bromo-2-iodopyrimidine [18]

and Re(CO)$_5$Br [19] were prepared by published procedures with modifications. Infrared spectra were measured on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. The ^{1}H NMR spectra were measured by using Bruker AMX400 spectrometers. Electronic absorption spectra were obtained on a Cary 50 prube UV–Vis spectrometer.

Emission spectra were recorded in deoxygenated solution at 298 K with a Hitachi F-4500 fluorescence spectrometer. The emission spectra were collected on samples with o.d. ~0.1 at the excitation wavelength. In all emission experiments, the sample solutions were filtered through 0.22 μm Millipore filters prior to measurement. UV–Vis spectra were checked before and after irradiation to monitor possible sample degradation. Emission maxima were reproducible to within 2 nm. Luminescence quantum yields (Φ_{em}) were calculated relative to [Ru^{II}(bpy)$_3$]Cl$_2$ in air-equilibrated aqueous solution ($\Phi_{em} = 0.028$) [20]. Luminescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%.

Room-temperature luminescence lifetimes were recorded on a SLM 48000S phase-modulation lifetime fluorescence spectrophotometer. The excitation light passed through a monochromator and was then intensity modulated at a different frequency by a Debye–Sears ultrasonic modulator. The sample and reference solutions were placed in a two-chamber turret. The emission intensities of each at the observation wavelength were approximately balanced by neutral density filters. The phase shift and modulation of each sample was measured alternately 25 times. The results were averaged and analyzed by an interfaced IBM computer. The errors forfitted lifetimes are estimated to be within 10%.

3.2. Synthesis of 4-(5-bromopyridine-2-ylethynyl)-benzonitrile (1)

5-Bromo-2-iodopyridine (0.284 g, 1.0 mmol), 4-ethynylbenzonitrile (0.140 g, 1.1 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (21.1 mg, 3 mmol%), CuI (11.7 mg, 6 mmol%), triphenylphosphine (6.6 mg, 2.5 mmol), diethylamine (10 mL) and THF (20 mL) were charged sequentially in a two-necked flask
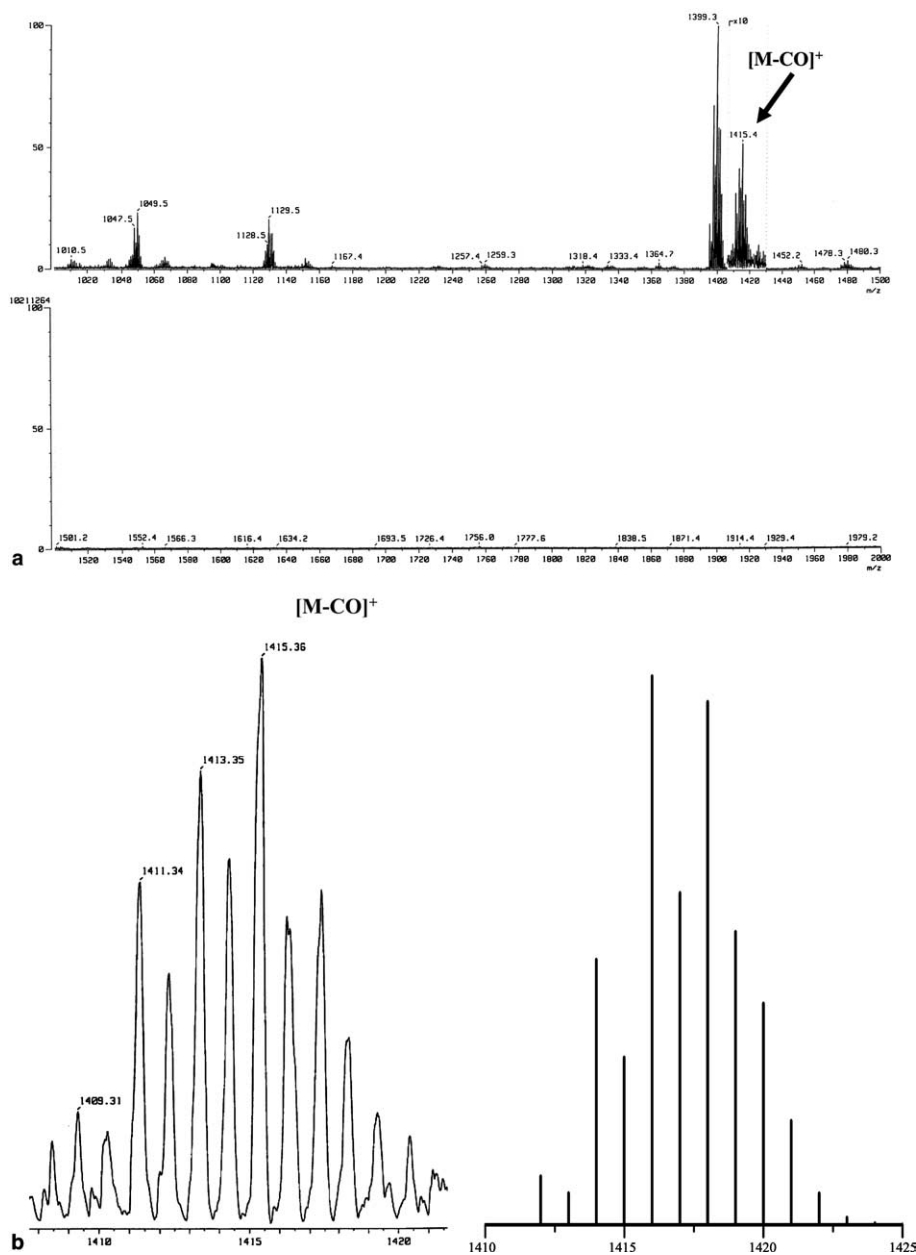
Fig. 2. (a) Full range FABMS spectra of complex **S3**. (b) Observed (left) and calculated (right) FABMS for complex **S3** fragment, $(M - CO)^+$.

under nitrogen atmosphere and heated to reflux for 24 h. After cooling, the volatiles were removed under vacuum, and the resulting solid was extracted into diethyl ether. The organic extract was washed with brine solution, dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent left a brown residue that was chromatographed through silica gel using dichloromethane/hexane mixture as eluant. Compound **1** was obtained as a white solid in 73% yield. MS (EI): m/e 283 (M^+); ^1H NMR ($CDCl_3$): 7.41 (d, $J = 8.3$ Hz, 1 H, NC*CH*), 7.62 (d, $J = 8.2$ Hz, 2 H, C_6H_4), 7.65 (d, $J = 8.2$ Hz, 2 H, C_6H_4), 7.83 (dd, $J = 2.4$, 8.4 Hz, 1 H, BrC*CH*), 8.67 (d, $J = 2.2$ Hz, 2 H, NC*H*); Anal. Calc. for $C_{14}H_7BrN_2$: C, 59.39; H, 2.49; N, 9.89. Found: C, 59.66; H, 2.35; N, 10.01%.

3.3. Synthesis of 4-(5-(4-diphenylaminophenyethynyl) pyridine-benzonitrile) (L1)

4-Ethynylphenyldiphenylamine (0.808 g, 6.0 mmol), 4-(5-bromopyridine-2-ylethynyl)benzonitrile (1.70 g, 3.0 mmol), $Pd(dba)_2$ (20 mg, 1 mmol%), t-BuONa (0.45 g, 4.5 mmol) and toluene (50 mL) were charged in a two-necked flask under nitrogen atmosphere, then $(t\text{-Bu})_3P$ (0.17 mL, 0.12 mmol, 0.706 M) was added after 10 min, and the solution was heated to reflux for 24 h. After cooling, the volatiles were removed under vacuum, and the resulting solid was extracted into diethyl ether. The organic extract was washed with brine solution, dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent left
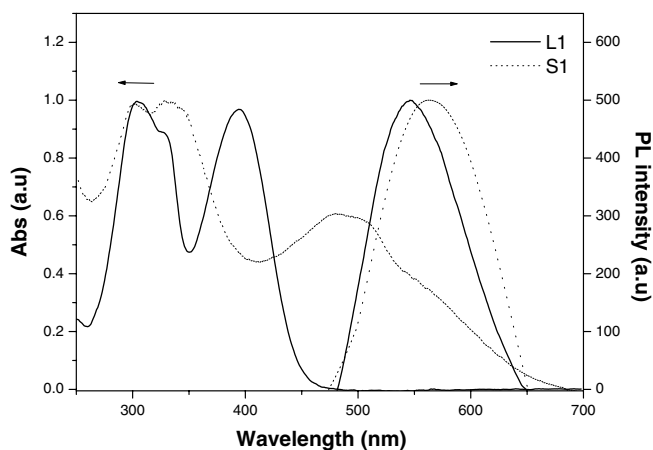
Fig. 3. Electronic absorption spectra and emission spectra of **L1** (solid line) and **S1** (dotted line) in CH$_2$Cl$_2$.

a brown residue that was chromatographed through aluminum oxide using ethyl acetate/hexane mixture (1:9) as eluant. Compound **L1** was obtained as a yellow solid in 65% yield. MS (FAB): *m/e* 472.1 (M + H)$^+$; ^{1}H NMR (CD$_2$Cl$_2$): 7.00 (d, *J* = 8.7 Hz, 2 H, NC$_6$H$_4$), 7.05–7.31 (m, 10 H, *aromatic*), 7.36 (d, *J* = 8.7 Hz, 2 H, NC$_6$H$_4$), 7.49 (d, *J* = 8.1 Hz, 1 H, NCC*H*). 7.63 (d, *J* = 8.6 Hz, 2 H, C$_6$H$_4$), 7.66 (d, *J* = 8.6 Hz, 2 H, C$_6$H$_4$), 7.77 (dd, *J* = 1.9, 8.0 Hz, 1 H, NCCH*CH*), 8.72 (d, *J* = 1.4 Hz, 1 H, N*CH*); Anal. Calc. for C$_{34}$H$_{21}$N$_3$: C, 86.60; H, 4.49; N, 8.91. Found: C, 86.32; H, 4.21; N, 8.88%; IR (*v*(CN), cm^{-1}): 2230 w.

3.4. Synthesis of supramolecule (*S1*)

The complex Re(CO)$_5$Br (406 mg, 1.0 mmol) was dissolved in THF solvent (50 mL) and heated to reflux for 24 h under nitrogen atmosphere. Complex Re(CO)$_3$-(THF)$_2$Br was formed during this time, then 4-(5-(4-diphenylaminophenyethynyl)pyridine-benzo-nitrile) (**L1**) (471 mg, 1.0 mmol) dissolved in THF was added via a cannula and heated to 60 °C for 24 h. After cooling, the volatiles were removed, and the residue was collected by filtration and washed thoroughly with ether, toluene, and hexane. Recrystallization of the crude product from dichloromethane/hexane gave complex **S1** as a purple solid in 92% yield. MS (FAB): *m/e* 1614.1 ((M – CO)$^+$, ^{187}Re; ^{81}Br); ^{1}H NMR (CD$_2$Cl$_2$): 6.95–7.47 (m, 28 H, *aromatic*), 7.76 (d, *J* = 8.5 Hz, 2 H, NCC*H*), 7.81 (d, *J* = 8.5 Hz, 8 H, C$_6$H$_4$), 8.45 (d, *J* = 8.4 Hz, 2 H, NCCH*CH*), 9.25 (d, *J* = 1.7 Hz, 2 H, N*CH*); Anal. Calc. for C$_{74}$H$_{42}$Br$_2$ N$_6$O$_6$Re$_2$: C, 54.08; H, 2.58; N, 5.11. Found: C, 54.41; H, 2.72; N, 4.98%; IR (*v*(CO), cm^{-1}): 2023 s, 1909 m, 1891 s; (*v*(CN), cm^{-1}): 2208 w.

3.5. Synthesis of (4-(5-naphthalen-1-yl-phenylamino)-pyridin-2-ylethynyl)benzonitrile (*L2*)

Naphthalen-yl-phenylamine (0.658 g, 6.0 mmol), 4-(5-bromopyridine-2-ylethynyl)benzonitrile (**1**) (1.70 g, 3.0

mmol), Pd(dba)$_2$ (20 mg, 1 mmol%), *t*-BuONa (0.45 g, 4.5 mmol) and toluene (50 mL) were charged in a two-necked flask under nitrogen atmosphere then (*t*-Bu)$_3$P (0.17 mL, 0.12 mmol, 0.706 M) was added after 10 min and heated to reflux for 24 h. After cooling, the volatiles were removed under vacuum, and the resulting solid was extracted into diethyl ether. The organic extract was washed with brine solution, dried over anhydrous MgSO$_4$ and filtered. Evaporation of the solvent left a brown residue that was chromatographed through aluminum oxide using ethyl acetate/hexane mixture (1:9) as eluant. Compound **L2** was obtained as a yellow solid in 60% yield. MS (FAB): *m/e* 422.1 (M + H)$^+$; ^{1}H NMR (CD$_2$Cl$_2$): 7.05–7.92 (m, 12 H, *aromatic*), 7.41 (dd, *J* = 2.0, 8.7 Hz, 1 H, NCCH*CH*), 7.59 (d, *J* = 8.2 Hz, 2 H, C$_6$H$_4$). 7.63 (d, *J* = 8.2 Hz, 2 H, C$_6$H$_4$), 7.84 (d, *J* = 8.3 Hz, 1 H, NCC*H*), 8.24 (d, *J* = 2.0 Hz, 1 H, N*CH*); Anal. Calc. for C$_{30}$H$_{19}$N$_3$: C, 85.49; H, 4.54; N, 9.97. Found: C, 85.38; H, 4.32; N, 9.72%; IR (*v*(CN), cm^{-1}): 2229 w.

3.6. Synthesis of 4-(5-bromopyrimidin-2-ylethynyl) benzonitrile (*2*)

5-Bromo-2-iodopyrimidine (0.29 g, 1.0 mmol), 4-ethynyl benzonitrile(0.140 g, 1.1 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (21.1 mg, 3 mmol%), CuI (11.7 mg, 6 mmol%), triphenylphosphine (6.6 mg, 2.5 mmol), diethylamine (10 mL) and THF (20 mL) were charged sequentially in a two-necked flask under nitrogen atmosphere and heated to reflux for 24 h. After cooling, the volatiles were removed under vacuum, and the resulting solid was extracted into diethyl ether. The organic extract was washed with brine solution, dried over anhydrous MgSO$_4$ and filtered. Evaporation of the solvent left a brown residue that was chromatographed through silica gel using dichloromethane/hexane mixture as eluant. Compound **2** was obtained as a white solid in 70% yield. MS (EI): *m/e* 283 (M$^+$); ^{1}H NMR (CDCl$_3$): 766 (d, *J* = 8.5 Hz, 2 H, C$_6$H$_4$), 7.73 (d, *J* = 8.5 Hz, 2 H, C$_6$H$_4$), 8.82 (s, 2 H, BrCC*H*); Anal. Calc. for C$_{13}$H$_6$BrN$_3$: C, 54.96; H, 2.13; N, 14.79. Found: C, 54.86; H, 2.15; N, 14. 43%.

3.7. Synthesis of 4-(5-diphenylaminopyrimidin-2-ylethynyl)-benzonitrile (*L3*)

Diphenylamine (1.02 g, 6.0 mmol), 4-(5-bromopyrimidin-2-ylethynyl)benzonitrile (**2**) (0.85 g, 3.0 mmol), Pd(dba)$_2$ (20 mg, 1.0 mmol%), *t*-BuONa (0.45 g, 4.5 mmol) and toluene (50 mL) were charged in a two-necked flask under nitrogen atmosphere, then (*t*-Bu)$_3$P (0.17 ml, 0.12 mmol, 0.706 M) was added after 10 min, and the solution was heated to reflux for 24 h. After cooling, the volatiles were removed under vacuum, and the resulting solid was extracted into diethyl ether. The organic extract was washed with brine solution, dried over anhydrous MgSO$_4$ and filtered. Evaporation of the solvent left a brown residue that was chromatographed through aluminum oxide using ethyl acetate/hexane mixture (1:9) as eluant. Compound **L3** was

obtained as a yellow solid in 50% yield. MS (FAB): m/e 373.1 $(M + H)^+$; ^1H NMR (CD$_2$Cl$_2$): 7.09–7.39 (m, 10 H, *aromatic*), 7.63 (d, $J = 8.3$ Hz, 2 H, C_6H_4), 7.70 (d, $J = 8.3$ Hz, 2 H, C_6H_4). 8.39 (s, 2 H, N*CH*); Anal. Calc. for C$_{25}$H$_{16}$N$_4$: C, 80.63; H, 4.33; N, 15.04. Found: C, 80.35; H, 4.37; N, 14.92%; IR (v (CN), cm^{-1}): 2228 w.

3.8. Synthesis of 4-(6-chloropyridine-3-ylethynyl)-benzonitrile (3)

5-Bromo-2-chloropyridine (0.193 g, 1.0 mmol), 4-ethynylbenzonitrile (0.140 g, 1.1 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (21.1 mg, 3 mmol%), CuI (11.7 mg, 6 mmol%), triphenylphosphine (6.6 mg, 2.5 mmol), diethylamine (10 mL) and THF (20 mL) were charged sequentially in a two-necked flask under nitrogen atmosphere and heated to reflux for 24 h. After cooling, the volatiles were removed under vacuum, and the resulting solid was extracted into diethyl ether. The organic extract was washed with brine solution, dried over anhydrous MgSO$_4$ and filtered. Evaporation of the solvent left a brown residue that was chromatographed through silica gel using dichloromethane/hexane mixture as eluant. Compound **3** was obtained as a white solid in 75% yield. MS (EI): m/e 239.8 $(M + H)^+$; ^1H NMR (CDCl$_3$): 7.34 (d, $J = 8.3$ Hz, 1 H, NC*CH*), 7.59 (d, $J = 8.5$ Hz, 2 H, C_6H_4), 7.64 (d, $J = 8.5$ Hz, 2 H, C_6H_4), 7.75 (dd, $J = 2.3$, 8.3 Hz, 1 H, Cl*CCH*), 8.53 (d, $J = 2.2$ Hz, 1 H, N*CH*); Anal. Calc. for C$_{14}$H$_7$ClN$_2$: C, 70.45; H, 2.96; N, 11.74. Found: C, 70.50; H, 2.99; N, 11.62%.

3.9. Synthesis of 4-(6-iodopyridine-3-ylethynyl)benzonitrile (4)

At 0 °C, hydroiodide (2.26 ml, 6 mmol) was added dropwise, over 30 min, to 4-(6-chloropyridine-3-ylethynyl)benzonitrile (3) (1.19 g, 5.0 mmol) in CH$_2$Cl$_2$ solvent (50 mL) for 16 h, then heated to 60 °C for 12 h. After cooling, K$_2$CO$_3$ and Na$_2$S$_2$O$_5$ were added to the flask. The mixture was extracted into dichloromethane. The organic extract was washed with brine solution, dried over anhydrous MgSO$_4$ and filtered. The volatiles were removed, and then the residue were dissolved in ether which was collected by filtration and the solvent were removed under vacuum. Compound **4** was obtained as a yellow solid. in 82% yield. MS (FAB): m/e 331.0 $(M + H)^+$; ^1H NMR (CDCl$_3$): 7.41 (dd, $J = 2.4$;8.3 Hz, 1 H, NCHC*CH*), 7.59 (d, $J = 8.2$ Hz, 2 H, C_6H_4), 7.63 (d, $J = 8.2$ Hz, 2 H, C_6H_4), 7.73 (d, $J = 8.2$ Hz, 1 H, NC*CH*), 8.49 (d, $J = 2.3$ Hz, 1 H, N*CH*); Anal. Calc. for C$_{14}$H$_7$IN$_2$: C, 50.94; H, 2.14; N, 8.49. Found: C, 51.12; H, 2.17; N, 8.43%.

3.10. Synthesis of 4-(6-(naphthalen-1-yl-phenylamino)pyrimidin-3-ylethynyl)benzonitrile (L4)

Naphthalenylphenylamine (0.658 g, 6.0 mmol), 4-(6-iodopyridin-3-ylethynyl)benzonitrile (4) (0.99 g, 3.0 mmol),

Pd(dba)$_2$ (20.0 mg, 1 mmol%), t-BuONa (0.45 g, 4.5 mmol) and toluene (50 mL) were charged in a two-necked flask under nitrogen atmosphere then (t-Bu)$_3$P (0.17 ml, 0.12 mmol, 0.706 M) was added after 10 min and heated to reflux for 24 h. After cooling, the volatiles were removed under vacuum, and the resulting solid was extracted into diethyl ether. The organic extract was washed with brine solution, dried over anhydrous MgSO$_4$ and filtered. Evaporation of the solvent left a brown residue that was chromatographed through aluminum oxide using ethyl acetate/hexane mixture (1:9) as eluant. Compound **L4** was obtained as a yellow solid in 62% yield. MS (FAB): m/e 422.0 $(M + H)^+$; ^1H NMR (CD$_2$Cl$_2$): 7.05–8.00 (m, 12 H, *aromatic*), 7.48 (d, $J = 8.1$ Hz, 1 H, NC*CH*), 7.59 (d, $J = 8.4$ Hz, 2 H, C_6H_4). 7.66 (d, $J = 8.4$ Hz, 2 H, C_6H_4) 7.74 (dd, $J = 2.3$;8.0 Hz, 1 H, NCHC*CH*), 8.31 (d, $J = 2.3$ Hz, 1 H, N*CH*); Anal. Calc. for C$_{30}$H$_{19}$N$_3$: C, 85.49; H, 4.54; N, 9.97. Found: C, 85.21; H, 4.45; N, 9.86%; IR (v(CN), cm^{-1}): 2230 w.

3.11. Synthesis of complexes S2, S3 and S4

Essentially the same procedure was used to obtain the complexes, so a detailed description is given above only for **S1**.

S2: Complex **S2** was obtained as a red solid in 88% yield. MS (FAB): m/e 1514.3 $((M - CO)^+$, ^{187}Re; ^{81}Br); ^1H NMR (CD$_2$Cl$_2$): 7.00–8.10 (m, 24 H, *aromatic*), 7.62 (d, $J = 8.1$ Hz, 8 H, C_6H_4). 7.66 (d, $J = 7.9$ Hz, 2 H, NCCH*CH*), 8.01 (d, $J = 8.2$ Hz, 2 H, NC*CH*), 8.60 (d, $J = 2.2$ Hz, 2 H, N*CH*); Anal. Calc. for C$_{66}$H$_{38}$Br$_2$N$_6$O$_6$Re$_2$: C, 51.37; H, 2.48; N, 5.45. Found: C, 51.02; H, 2.35; N, 5.56%; IR (v(CO), cm^{-1}): 2026 s, 1923 m, 1906 s; (v(CN), cm^{-1}): 2210 w.

S3: Complex **S3** was obtained as dark red solid. in 67% yield. MS (FAB): m/e 1415.4 $((M - CO)^+$, ^{187}Re; ^{81}Br), 1364.8 $((M - Br)^+$, ^{187}Re; ^{81}Br); ^1H NMR (CD$_2$Cl$_2$): 7.00–7.42 (m, 20 H, *aromatic*), 7.66 (d, $J = 8.2$ Hz, 4 H, C_6H_4), 7.74 (d, $J = 8.2$ Hz, 4 H, C_6H_4). 8.40 (s, 2 H, N*CH*). 8.52 (s, 2 H, N*CH*); Anal. Calc. for C$_{56}$H$_{32}$Br$_2$N$_8$O$_6$Re$_2$: C, 46.54; H, 2.23; N, 7.75. Found: C, 46.98; H, 2.02; N, 7.43%; IR (v(CO), cm^{-1}): 2024 s, 1924 m, 1890 s; (v(CN), cm^{-1}): 2209 w.

S4: Complex **S4** contaminated with some impurities were obtained as a orange solid. MS (FAB): m/e 1193.7 $((M + H)^+$, ^{187}Re; ^{81}Br), 1113.8 $((M - Br)^+$, ^{187}Re; ^{81}Br); ^1H NMR (CD$_2$Cl$_2$): 7.50 (d, $J = 8.4$ Hz, 2 H, NC*CH*), 7.80 (d, $J = 8.3$ Hz, 2 H, NCHC*CH*), 8.29 (s, 2 H, N*CH*); Anal. Calc. for C$_{63}$H$_{38}$BrN$_6$O$_3$Re: C, 63.42; H, 3.21; N, 7.04. Found: C, 65.06; H, 3.98; N, 6.32%; IR (v(CO), cm^{-1}): 2024 s, 1909 m, 1892 s; (v(CN), cm^{-1}): 2213 w.

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