Construction of hexanuclear macrocycles by a coupling strategy from polyfunctionalized bis(terpyridines)†‡

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The construction of a heteronuclear (Ru_4Fe_2) hexameric metallomacrocycle with methyl- and carbonyl-functionalized bis(terpyridyl) moieties was achieved by a self-assembly of a dinuclear trimer, which was prepared in high yield *via* Pd(0) coupling of a bis-iodo functionalized dinuclear complex with a terpyridine possessing an acetylene group.

Introduction

There has been considerable research conducted on octahedral terpyridine transition metal complexes, especially regarding the fine-tuning of their electrochemical, photophysical and optical properties, as well as precursors to build supramolecular architectures.[1] However, functionalized terpyridine complexes have been, by and large, underutilized relative to their unsubstituted counterparts due to their limited accessibility and the generally poor yields of metal complexation, even though they have been shown to possess interesting luminescent properties.[2–6] They have also been utilized as chemosensors,[7,8] fluorescent immunoassay agents,[9–12] as well as catalysts[13–16] and dye-synthesized solar cells.[17–22]

Carboxylic acids or carboxylates have been the favored terpyridine functional groups, since they play a crucial role for surface anchoring as well as act as potential internal counterions. For example, a black dye containing a terpyridine with three carboxylates was attached to nanocrystalline TiO_2 surface for use as a solar cell that demonstrated an overall conversion efficiency of 10.4% (Fig. 1).[18] Carboxylate groups have also been introduced at the 4-position of terpyridine Ru(II) complex ($[Ru(4'\text{-phenyl-4-carboxylate-2,2':6',2''\text{-terpyridine})_2]^0$) in order to promote a photoinduced electron transfer *via* ionic interactions with methyl viologen.[23]

The construction of "benzenoid-based" metallomacrocycles was achieved *via* either a one-pot self-assembly or step-wise sequence from 120° juxtaposed bis(terpyridine) ligands and various transition metals [Fe(II), Ru(II), Zn(II); Scheme 1].[24–31] These supramolecular architectures displayed luminescence properties when constructed with Zn(II),[29,30] electrostatically attached to multi-wall carbon nanotubes,[31,32] and utilized as a molecular nanotemplate.[33]

In this work, the synthesis and characterization of functionalized mononuclear Fe(II) and Ru(II) complexes (**25–28** and **33–39**, respectively), as well as the preparation of tetra(ethoxycarbonyl)-bis(terpyridine) **15** and tetramethyl-bis(terpyridine) **8** and **9** *via* Pd[0]-coupling and Kröhnke[34] method, respectively, are discussed. The facile and high yield complexation procedures of dimethylterpyridines with di(ethoxycarbonyl)terpyridine **32** were used as a basic strategy to prepare dinuclear complexes **40** and **44**, which are the precursors for the dinuclear trimer **46**. An alternative coupling route to construct the functionalized dinuclear complex **44**, which was used as a precursor to assemble a hexanuclear metallomacrocycle **47** containing mixed metals (Ru_4Fe_2) and three different terpyridinyl moieties with eight methyl and eight ethoxycarbonyl groups, will be presented. The single-crystal X-ray structures of bis(terpyridine) **9** and homoleptic complex **38** are also presented.

Results and discussion

Synthesis of tetramethyl substituted bis(terpyridines) **8** and **9** was achieved *via* a two-step Kröhnke[34] procedure (Scheme 2). Treatment of dialdehydes **2** and **5** with four equivalents of 2-acetyl-4-methylpyridine gave bis(diketone) intermediates **6** and **7**, respectively, then the ring-closure of these intermediates in the presence of NH_4OAc and AcOH afforded the desired bis(terpyridines) **8** and **9** in albeit poor yields (6–13%). Proton resonances (^1H NMR) for the terpyridinyl moieties of ligands **8** and **9** showed upfield shifts for 5,5″-, 6,6″- and 3,3″-tpy*H*s ($\Delta\delta$ = 0.16–0.23) compared to 1,3-bis(2,2′:6′,2″-terpyridin-4′-yl)-5-R-benzene[25] (R = Br, Me) due to shielding effect of four electron-donating methyl moieties. The HRMS spectra of **8** further confirmed its structure by a single peak at m/z = 675.1850 $[M + H]^+$.

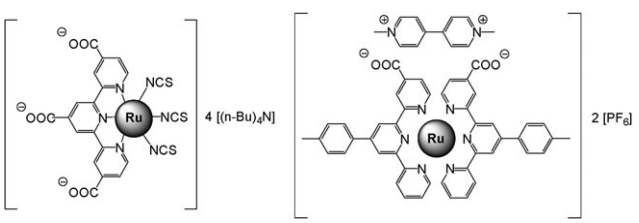

Fig. 1 Structures of carboxylate functionalized Ru(II)-terpyridine complexes.[18,23]

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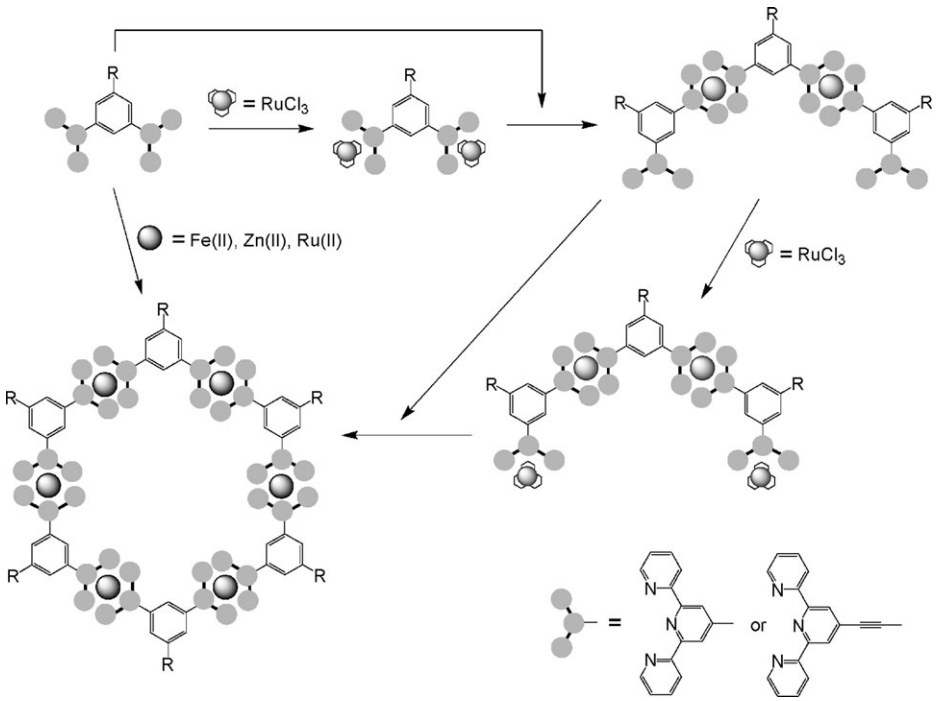
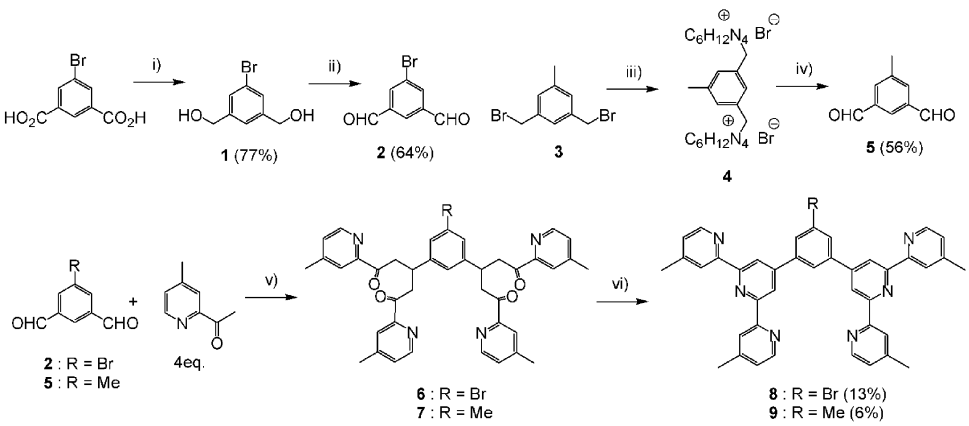


Scheme 1 The construction of hexanuclear metallomacrocycles *via* either self-assembly or a step-wise manner.[24–31]



Scheme 2 Synthesis of bis(terpyridines) **8** and **9** *via* the Kröhnke[34] method. *Reagents and conditions*: (i) BH_3·THF, THF, 25 °C, 10 h; (ii) PCC, DCM, 25 °C, 2 h; (iii) HTMA, $CHCl_3$, 70 °C, 1 h, N_2; (iv) AcOH/H_2O (1 : 9), 98 °C, 1 h, N_2; (v) NaOH (4 M), MeOH, 25 °C, 9 h; (vi) AcOH, NH_4OAc, 110 °C, 11 h.

The single-crystal X-ray structure of ligand **9** confirmed the proposed structure (Fig. 2). The three pyridine rings showed a *transoid* arrangement about the interannular C–C bonds, which was in agreement with the literature.[35–38] This configuration minimizes electrostatic interactions between the nitrogen lone pairs and van der Waals interactions between the *meta* protons.[35] The interannular C–C bond lengths of bis(terpyridine) **9** [1.487(8)–1.496(4) Å] are comparable with terpyridines [1.480(1)–1.498(3) Å] found in the literature.[35–37] The three pyridine rings are not exactly coplanar and the torsion angles of two terminal rings with the central pyridine ring are 13.08, 19.72 and 8.34, 12.08° for each terpyridine moiety of **9**, which are higher than 4′-(4-bromophenyl)-4,4″-dimethylterpyridine[39] (9.48 and 1.06°). The central benzene ring connected to the terpyridines is also distorted

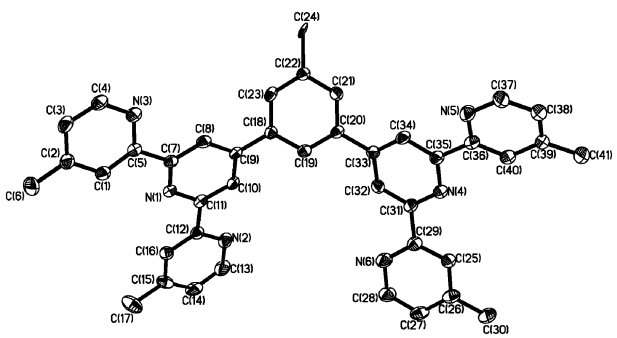
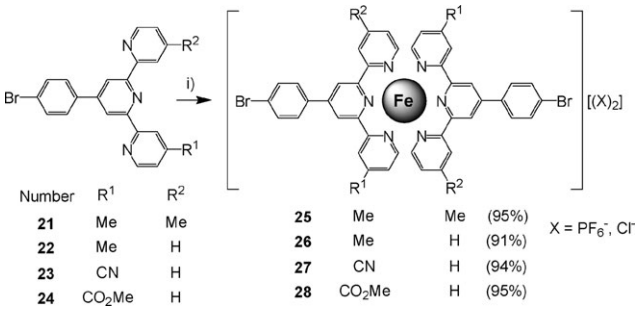


Fig. 2 ORTEP drawing of bis(terpyridine) 9 with atoms shown at 50% probability.

with torsion angles of 57.53 and 36.61°, which are comparable to that of 4′-(4-bromophenyl)-4,4″-dimethylterpyridine[39] (39°) and 4′-(2,5-dimethoxyphenyl)terpyridine[40] (50.4°).

Preparation of the bis(terpyridines) **14** and **15** was achieved *via* Pd[0]-mediated cross-coupling[41] of terpyridines **12** and **13** with 1,3-diethynyltoluene[42] (**10**, Scheme 3). Proton resonances (^{1}H NMR) for the terpyridinyl moiety of the ligand **15** showed downfield shifts for the 5,5″-tpy*H* (δ = 7.94, $\Delta\delta$ = 0.58) and 3,3″-tpy*H* (δ = 9.22, $\Delta\delta$ = 0.52) compared to bis(terpyridine) **14** due to deshielding effect of four electron-withdrawing ethoxycarbonyl moieties. The HRMS spectra of **14** and **15** further confirm their structures by single peaks at m/z = 755.2910 and 1043.3726 $[M + H]^+$, respectively. Terpyridines **17** and **20** containing free acetylene functionality were prepared by fluoride-based removal of the deprotected trimethylsilyl groups on terpyridines **19** and **16**, which were each synthesized *via* Pd[0]-mediated coupling of the aryl iodide **13** with **11** and **18** with $Me_3Si–C\equiv CH$, respectively. Structures of terpyridines **16–20** were confirmed by ^{1}H, ^{13}C, COSY NMR and HRMS spectroscopy (experimental section).

Treatment of functionalized terpyridines **21–24** with 0.5 equivalence of $FeCl_2{\cdot}4H_2O$ in MeOH gave a purple solution that was concentrated *in vacuo* and dried to afford complexes **25–28** (Scheme 4) in >90% yield. The ^{1}H NMR spectra of these complexes displayed a characteristic upfield shift of 6,6″-tpy*H* ($\Delta\delta$ = 1.25–1.59) compared to the ligands because the 6,6″-protons are located above-the-plane of the aromatic ring of the adjacent ligand. The complexes **26–28** containing unsymmetrical ligands showed unique proton resonances for each pyridine ring as a result of diminished symmetry. The disubstituted complexes **26–28** are believed to be structurally chiral because these octahedral complexes are

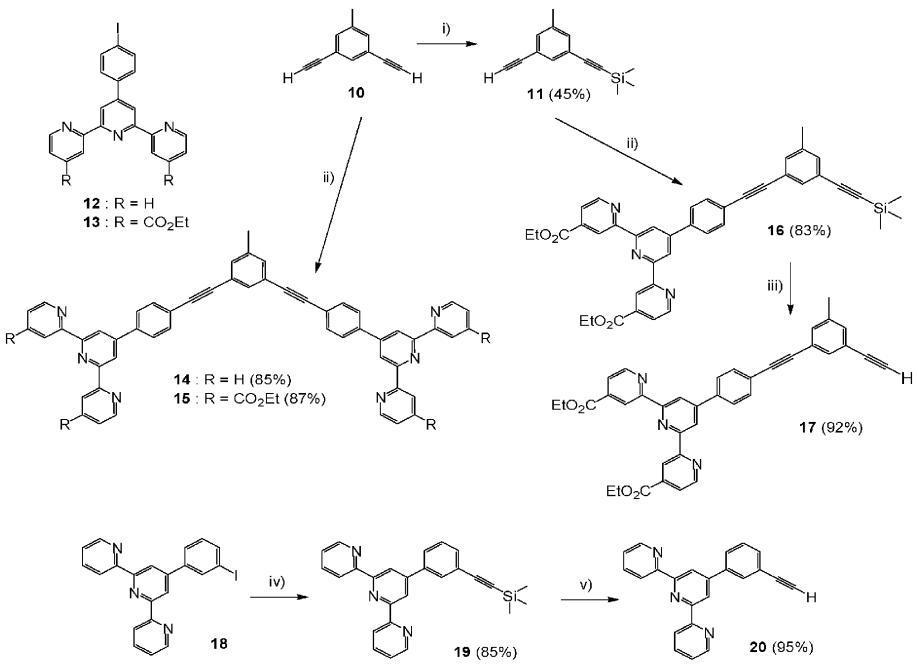


Scheme 4 Synthesis of mononuclear Fe(II)-complexes **25–28**. *Reagents and conditions*: (i) $FeCl_2{\cdot}4H_2O$, MeOH, 60 °C, 8–20 h, then NH_4PF_6.

not superimposable on their mirror images; however, attempts to separate the structural isomers were unsuccessful. The structures of **25–28** were established *via* HRMS and ESI-MS by the unique signals at m/z = 444.0342, 430.0191, 441.0 and 473.0 corresponding to $[M - 2Cl]^{2+}$, respectively, as well as their ^{1}H NMR spectra.

The UV-Vis spectra of these complexes revealed a characteristic MLCT band at 570–577 nm in MeOH at 25 °C (Fig. 3). This absorption lies in the visible region and is responsible for the intense purple color of the complexes. Complexes **27** and **28** containing electron-withdrawing cyano and methoxycarbonyl groups displayed a slightly blue shifted MLCT (7 nm) when compared to complexes **25** and **26** with electron-donating methyl groups.

Homoleptic Ru(II)-terpyridine complexes **33** and **34** were obtained by refluxing the dimethylterpyridine **21** and di(methoxycarbonyl)terpyridine **30** with 0.5 equivalents of $RuCl_3{\cdot}3H_2O$ in MeOH under reducing conditions (*N*-ethylmorpholine) for



values.

Scheme 3 Synthesis of bis(terpyridines) **14** and **15** and terpyridines **16**, **17**, **19** and **20** *via* coupling strategy. *Reagents and conditions*: (i) *n*-BuLi, Me_3SiCl, THF, −78 °C, 6 h, N_2; (ii) **12** or **13**, $Pd(PPh_3)_4$, CuI, THF/NEt_3, 80 °C, 11 h, (iii) KF, THF/EtOH, 25 °C, 10 h; (iv) $Me_3SiC\equiv CH$, $Pd(PPh_3)_4$, CuI, THF/NEt_3, 80 °C, 11 h, argon; (v) $(n\text{-}Bu)_4NF{\cdot}3H_2O$, THF, 25 °C, 6 h.

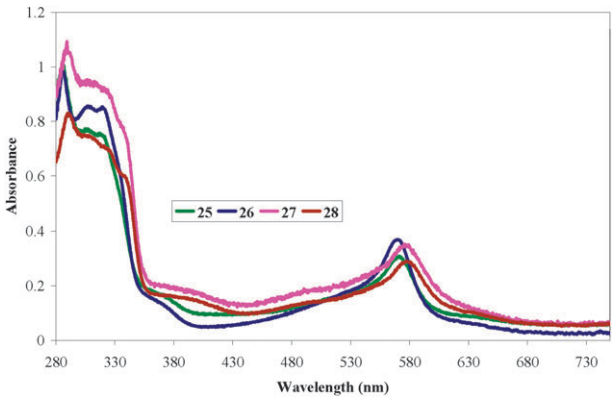


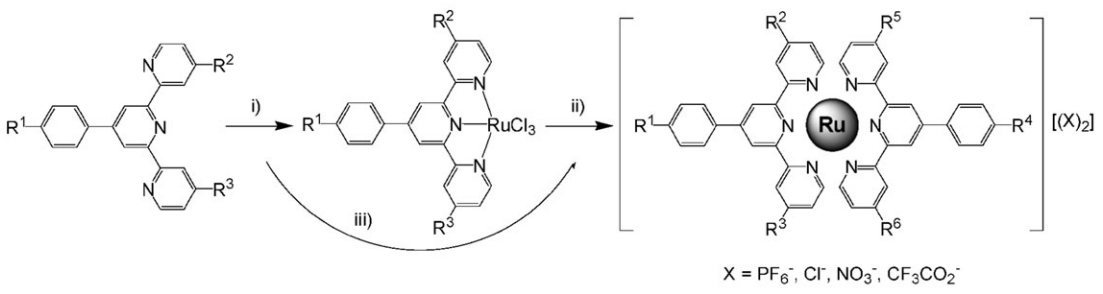
Fig. 3 UV-Vis spectra of Fe(II)-terpyridine complexes **25–28** in MeOH at 25 °C.

10 and 20 h, respectively (Scheme 5). The lower reaction yield of **34** (40%) compared to **33** (98%) was rationalized by the insolubility of the ligand **30**. Although terpyridines possessing electron-withdrawing groups should lead to weaker complexes, to address the solubility issue, the di(methoxycarbonyl) groups were converted to di(ethoxycarbonyl) analogs, as in **29** and **13**. The metalated adducts **31** and **32** were prepared by treating these terpyridines with $RuCl_3{\cdot}3H_2O$ (>1 eq.) in >80% yields. The adduct **32** was treated with one equivalent of ligand **13** under reducing conditions (*N*-ethylmorpholine) to give homoleptic complex **38** in 55% yield. The yield was finally optimized when the adduct **31** was treated with dimethyl ligand **21** affording the heteroleptic complex **36** in nearly quantitative yield. The complexes **33**, **34**, **36** and **38** exhibited a characteristic upfield shift (^{1}H NMR) for the 6,6″-tpy*H* ($\Delta\delta$ = 1.22–1.30) compared to the free ligands; moreover, heteroleptic **36** displayed two different sets of terpyridine peaks. Mass spectral data (HRMS) of **33–39** were also in accord with the assigned structures and isotope patterns of the peaks perfectly matched the theoretical values.

The methoxy- and ethoxycarbonyl groups in **34**, **36** and **38** were hydrolyzed with aqueous NaOH (1 M, excess) in DMF at 60 °C for 12 hours affording the corresponding sodium carboxylate salts, which were protonated (TFA) to give the desired carboxylic acid terpyridine complexes **35**, **37** and **39**, respectively, in >90% yields. The ^{1}H NMR spectra of these acids were identical to their starting ester complexes except they did not contain methoxy- or ethoxycarbonyl peaks.

Single crystals of homoleptic complex **38**$[(PF_6)_2]$ were grown in MeCN and the X-ray analysis (100 K) confirmed the proposed pseudo-octahedral structure (Fig. 4A). The crystal is orthorhombic with space group $P2_12_12_1$ and each complex has two PF_6^- ions and one MeCN in the lattice. The angle of N(1)–Ru(1)–N(2) is 178° and the mean angle between the two terpyridines is 92.8°; thus, the two terpyridines are tilted 2–2.8° away from perfect orthogonality. The torsion angles of two terminal pyridine rings with central pyridine ring are between 1.14–3.60°, which are almost perfectly coplanar. The edge-to-edge distances of the complex **38** are 20 and 22 Å (Fig. 4B). The shortest distance between Ru(II) metals is 10.1 Å in the lattice and Ru(II) metal centers are 4.88 and 7.18 Å away from MeCN and PF_6^-, respectively.

The molecular packing of crystals of **38** did not show any π–π interactions between aromatic rings (Fig. 4C); however, it revealed short distances between I···O=C (3.15–3.2 Å) when visualized along *b* axis (Fig. 5). These short iodo-carbonyl interactions dominated the lattice and played a crucial role in the crystallization process, while MeCN molecules did not show any bonding.



Number	R1	R2	R3	Number	R1	R2	R3	Number	R1	R2	R3	R4	R5	R6	
29	Br	CO_2Et	CO_2Et	**31**	Br	CO_2Et	CO_2Et	**33**	Br	Me	Me	Br	Me	Me	
13	I	CO_2Et	CO_2Et	**32**	I	CO_2Et	CO_2Et	**34**	Br	CO_2Me	CO_2Me	Br	CO_2Me	CO_2Me	iv)
21	Br	Me	Me					**35**	Br	CO_2H	CO_2H	Br	CO_2H	CO_2H	
30	Br	CO_2Me	CO_2Me					**36**	Br	CO_2Et	CO_2Et	Br	Me	Me	iv)
								37	Br	CO_2H	CO_2H	Br	Me	Me	
								38	I	CO_2Et	CO_2Et	I	CO_2Et	CO_2Et	iv)
								39	I	CO_2H	CO_2H	I	CO_2H	CO_2H	

Scheme 5 Synthesis of mononuclear Ru(II)-complexes **35–41**. *Reagents and conditions*: (i) **29** or **13**, $RuCl_3{\cdot}3H_2O$ (>1 eq.), EtOH/THF, 70 °C, 15 h; (ii) **13**, or **21**, *N*-ethylmorpholine, EtOH, 70 °C, 10–24 h, then NH_4PF_6; (iii) **21** or **30**, $RuCl_3{\cdot}3H_2O$ (0.5 eq.), *N*-ethylmorpholine, MeOH, 70 °C, 10–20 h; (iv) NaOH (1 M), DMF, 60 °C, 12 h, TFA.

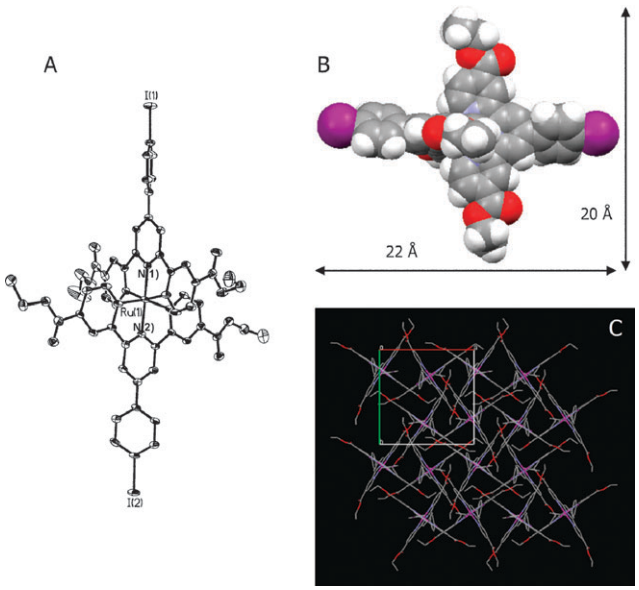


Fig. 4 (A) Single-crystal X-ray structure of **38**[$(PF_6)_2$] (atoms drawn at 50% probability), (B) its space filling model, and (C) molecular packing (along *c* axis); MeCN and PF_6^- are omitted for clarity.

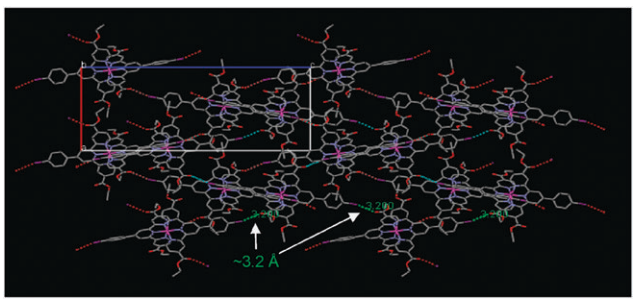


Fig. 5 Molecular packing of crystals of **38** (along *b* axis); MeCN and PF_6^- are omitted for clarity.

The UV-Vis spectra of tetramethyl Ru(II)-complex **33** displayed the characteristic MLCT peak at 493 nm; whereas, the MLCT for carbonyl Ru(II)-complexes **35–39** appeared at 503 nm in MeCN at 25 °C (Fig. 6). These absorptions lie in the visible region and are responsible for the intense red color of the complexes. The hypsochromic shift (10 nm) of MLCT of complex **33** compared to **35–39** is due to its electron-donating four methyl moieties. Further, MLCT band (503 nm) of complexes **36** and **37** showed a shoulder at *ca.* 490 nm because of the two methyl moieties.

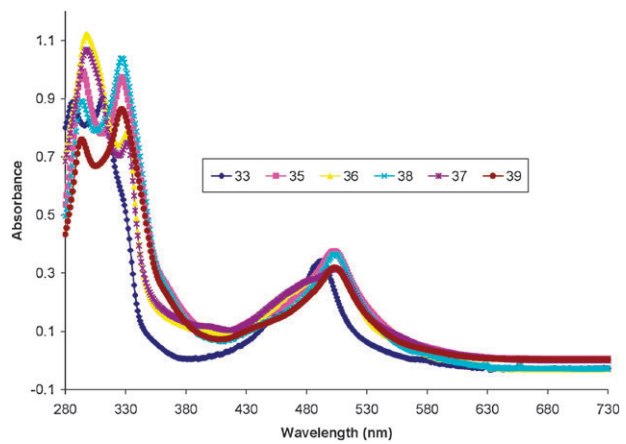
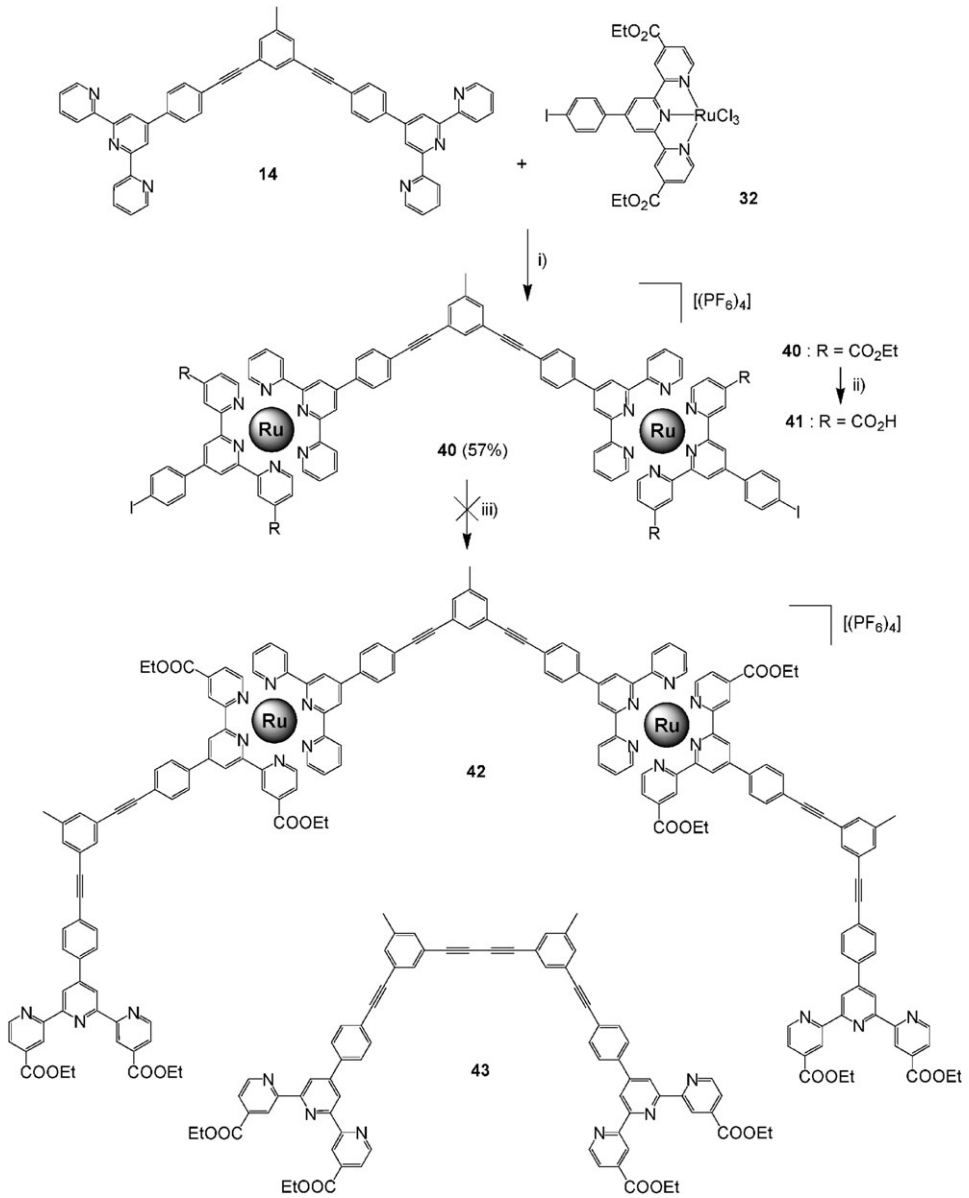


Fig. 6 UV-Vis spectra of Fe(II)-terpyridine complexes **33–39** in MeCN at 25 °C.

The construction of dinuclear Ru(II)-complexes **40** and **44** containing di-iodo functionality was achieved by treating bis(terpyridines) **14** and **8** with two equivalents of the metalated adduct **32**, respectively, under reducing conditions (*N*-ethylmorpholine, Scheme 6 and Scheme 7). The reaction mixture of **14** and **32** was chromatographed (SiO_2) eluting with MeCN–sat. KNO_3 (aq)–H_2O (20 : 1 : 1) then the counterion was exchanged by treating with an excess NH_4PF_6 (1 M) to afford the desired dinuclear **40**[$(PF_6)_2$] in 57% yield. On the other hand, dimetallic **44**[$(Cl)_2$] was obtained in quantitative yield by just *in vacuo* removing the solvent and drying the residue. The ^{1}H NMR spectra of **40**[$(PF_6)_2$] in CD_3CN and **44**[$(Cl)_2$] in CD_3OD displayed two set of proton peaks for each terpyridine moiety with 1 : 1 proton integration ratio supporting the dinuclear structures and they also showed the characteristic upfield and downfield shifts for 6,6″-tpy*H* ($\Delta\delta$ = 1.20–1.35) and 3′,5′-tpy*H* ($\Delta\delta$ = 0.33–0.54), respectively. Moreover, complex **44** revealed notable downfield shifts for 4,6-Ben*H* ($\Delta\delta$ = 0.62) and 2-Ben*H* ($\Delta\delta$ = 0.77). The structure of **40**[$(PF_6)_2$] was further confirmed with HRMS by the unique signal at *m*/*z* 529.0571 corresponding to $[M - 2PF_6]^{2+}$, and isotope patterns of the peak perfectly matched the theoretical values. Later, the dinuclear **40** and **44** were hydrolyzed by treatment with aqueous NaOH (1 M, excess) in DMF at 60 °C for 12 h affording sodium carboxylate salts, which were protonated in the presence of TFA to give carboxylic acid functionalized complexes **41** and **45** in >90% yield. The ^{1}H NMR spectra of these acids were identical to their starting ester complexes except they did not contain proton peaks for $CO_2CH_2CH_3$. The UV-Vis spectra of dinuclear complexes **40**, **41**, **44** and **45** displayed the characteristic MLCT peak at *ca.* 501–507 nm in MeCN at 25 °C.

The initial attempt to prepare the dinuclear complex **42** containing two free terpyridinyl moieties *via* Pd[0]-coupling strategy was unsuccessful (Scheme 6). The terpyridine **17** containing a free acetylene group was intended to couple with bis-iodo functionality of dinuclear **40** in the presence of $Pd(PPh_3)_4$/CuI in THF/MeCN/NEt_3 under argon; however, the free acetylene of **17** coupled *via* CuI catalysis with another acetylene of **17** to give the bis(terpyridine) **43** in 64% yield and unreacted starting material **40**. The ^{1}H NMR spectrum of bis(terpyridine) **43** displayed similar proton resonances to that of starting ligand **17**, except lacking an acetylenic proton. The structure of **43** was further confirmed *via* HRMS by the unique signal at *m*/*z* = 1181.4253 corresponding to $[M + H]^+$.

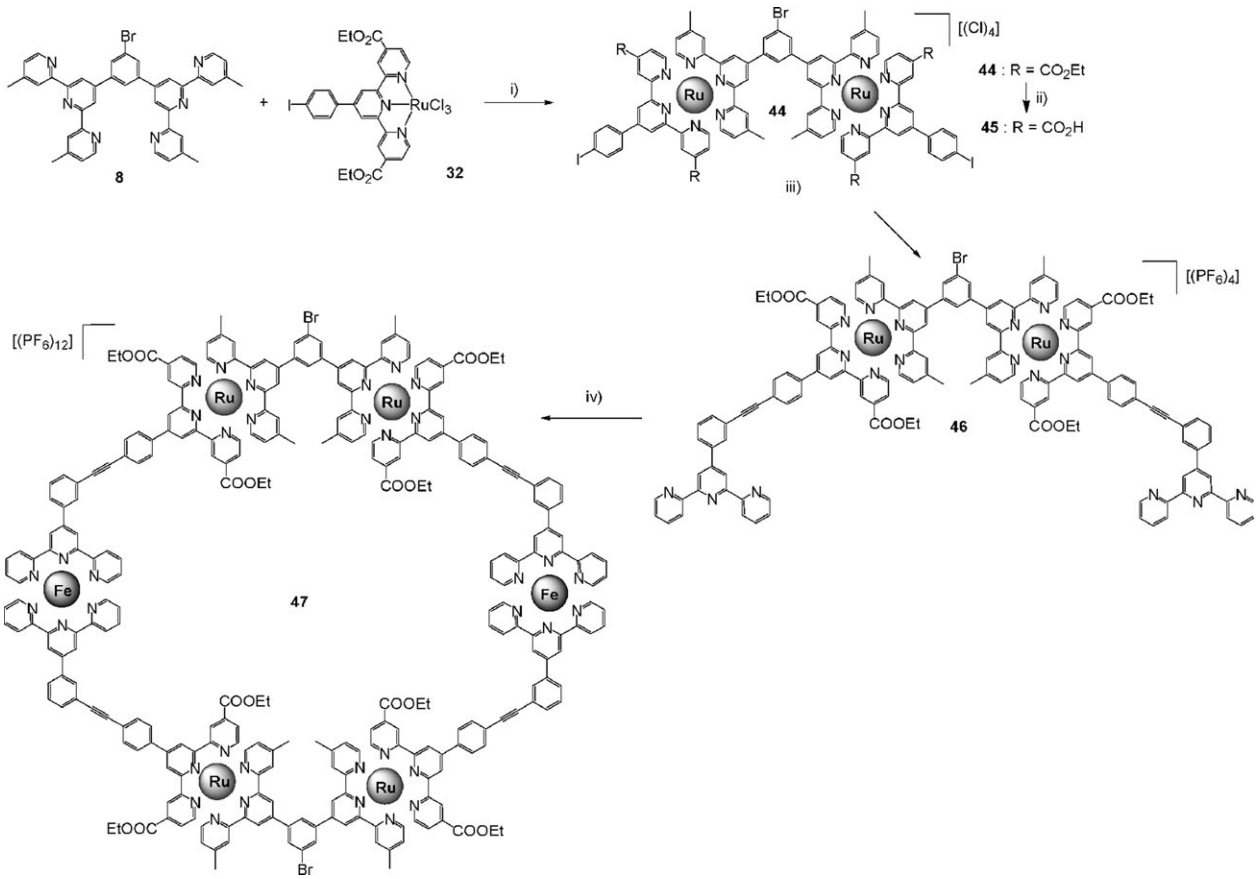
The construction of dinuclear **46**, which was functionalized with two terpyridinyl moieties, was achieved by treating the dinuclear **44** with two equivalents of ligand **20** in presence of $Pd(PPh_3)_4$ in DMF/NEt_3. Copper catalysis (CuI) was intentionally omitted to circumvent the acetylene-acetylene coupling of the ligand **20**. The separation of dinuclear **46** from other by-products was accomplished by loading the concentrated reaction mixture on a preparative TLC plate (SiO_2)



Scheme 6 Synthesis of dinuclear Ru(II) **40** and **41** and bis(terpyridine) **43**. *Reagents and conditions*: (i) *N*-ethylmorpholine, EtOH, 70 °C, 24 h, then NH_4PF_6; (ii) NaOH (1 M), DMF, 60 °C, 12 h, TFA; (iii) **17**, $Pd(PPh_3)_4$, CuI, THF/MeCN/NEt_3, 70 °C, 12 h, argon.

eluting with a solvent mixture of MeCN–sat. KNO_3 (aq)–H_2O (7 : 1 : 1). The darkest band (3rd line from the top) was removed from the plate and washed with the eluting solvent, followed by counterion exchange by the addition of excess NH_4PF_6 (1 M) to afford the desired dinuclear **46**$[(PF_6)_4]$ in 35% yield (Scheme 7). The ^{1}H NMR of the bis(Ru^{II}) trimer **46** displayed three sets of terpyridine proton resonances, two for complexed terpyridines and one for free terpyridine, with a 1 : 1 : 1 5,5″-terpyridine proton integration ratio confirming the two iodo-acetylene couplings (Fig. 6B). The 2D correlation NMR experiments (COSY) were conducted to ensure the proper assignments. The first band from the preparative TLC plate was also collected and found to be a mono-coupling product in 24% yield rationalizing the poor yield of the trimer **46**. The UV-Vis spectra of trimer **46** displayed the characteristic MLCT peak at 508 nm in MeCN at 25 °C, which is similar to dinuclear **44** (507 nm).

The self-assembly of hexanuclear macrocycle **47**$[(PF_6)_{12}]$ was achieved by treating the trimer **46**$[(PF_6)_4]$ with an equimolar amount of $FeCl_2{\cdot}4H_2O$ in EtOH and acetone (Scheme 7). The macrocycle **47** was obtained in 24% yield after purifying with a preparative TLC plate (SiO_2) eluting with a solvent mixture of MeCN–sat. KNO_3 (aq)–H_2O (7 : 1 : 1). This heteronuclear macrocycle contains four Ru(II) and two Fe(II) metals with eight methyl and eight ethoxycarbonyl groups. The ^{1}H NMR of the macrocycle **47** displayed three sets of terpyridine proton resonances with 5,5″-terpyridine proton integration ratio of 1 : 1 : 1 and did not contain any free terpyridine proton peaks. Further, 6,6″-tpy$_3$*H* and 3′,5′-tpy$_3$*H* protons of **47** displayed the characteristic upfield ($\Delta\delta$ = 0.65) and downfield shifts ($\Delta\delta$ = 0.39), respectively, compared to the dinuclear **46** (Fig. 7). The UV-Vis spectrum of the macrocycle **47** further confirmed the proposed structure by revealing two different



Scheme 7 Synthesis of dinuclear Ru(II) **44–46**, and hexanuclear Ru(II)-Fe(II) **47**. *Reagents and conditions*: (i) *N*-ethylmorpholine, EtOH, 70 °C, 9 h; (ii) NaOH (1 M), DMF, 60 °C, 12 h, TFA; (iii) **20**, $Pd(PPh_3)_4$, DMF/NEt_3, 70 °C, 48 h, argon, then NH_4PF_6; (iv) $FeCl_2{\cdot}4H_2O$, EtOH/acetone, 60 °C, 20 h, then NH_4PF_6.

MLCT absorptions for Ru(II) and Fe(II) at 511 and 569 nm, respectively, in MeCN at 25 °C. The absorbance ratio of Ru(II)-MLCT (511 nm)/Fe(II)-MLCT (569 nm) is 2.42 suggesting the 4.8 : 2 metal ratio in the macrocycle **47**.

Conclusions

The 4,4″-dimethyl functionalized bis(terpyridine)s **8** and **9** were synthesized *via* the Kröhnke method and a single crystal X-ray structure of **9** was obtained. A novel 4,4″-di(ethoxycarbonyl) functionalized bis(terpyridine) **15** was prepared *via* Pd[0]-mediated cross-coupling method. The synthesis of heteroleptic Ru(II) complex **36** was accomplished in a quantitative yield; whereas, homoleptic complexes **34** and **38** were obtained in only moderate yields. The single-crystal X-ray structure of the homoleptic complex **38** revealed iodo-carbonyl interactions. The high yield complexation reactions of the carbonyl-functionalized metalated adduct **32** with methyl substituted mono- and bis-terpyridines were adapted, as a main strategy, to construct a bis-iodo functionalized dinuclear **44**, which was coupled with terpyridine **20** containing a free acetylene group to form the dinuclear trimer **46**. The heteronuclear (Ru_4Fe_2) metallomacrocycle **47** was finally assembled by treatment of the trimer **46** with an equimolar amount of $FeCl_2{\cdot}4H_2O$. The carboxylic acid functionalized Ru(II) complexes were prepared to investigate their solar cell applications and supramolecular aggregation behavior through hydrogen-bonding.

Experimental

General comments

Melting point data were obtained in capillary tubes with an Electrothermal 9100 melting point apparatus and are uncorrected. All chemicals were purchased from Aldrich Co. Tetrahydrofuran (THF) was dried by refluxing over benzophenone/Na under N_2. Dichloromethane was dried over CaH_2. All other commercially available solvents were used without further purification. Column chromatography was conducted using silica gel (60–200 mesh) from Fisher Scientific with the stipulated solvent mixture. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$, except where noted, and are recorded at 250 and 52 MHz, respectively. Infrared spectra (IR) were obtained (KBr pellet, unless otherwise noted) and recorded on an ATI Mattson Genesis Series FTIR spectrometer. Mass spectral data were obtained using an Esquire electrospray ionization mass spectrometer (ESI) and are reported as: (assignment, relative intensity); ESI samples were typically prepared in MeOH–H_2O–TFA (70 : 30 : 01) for positive ion mode or Me_2CHOH–H_2O–NH_3 (70 : 30 : 1) for negative ion mode

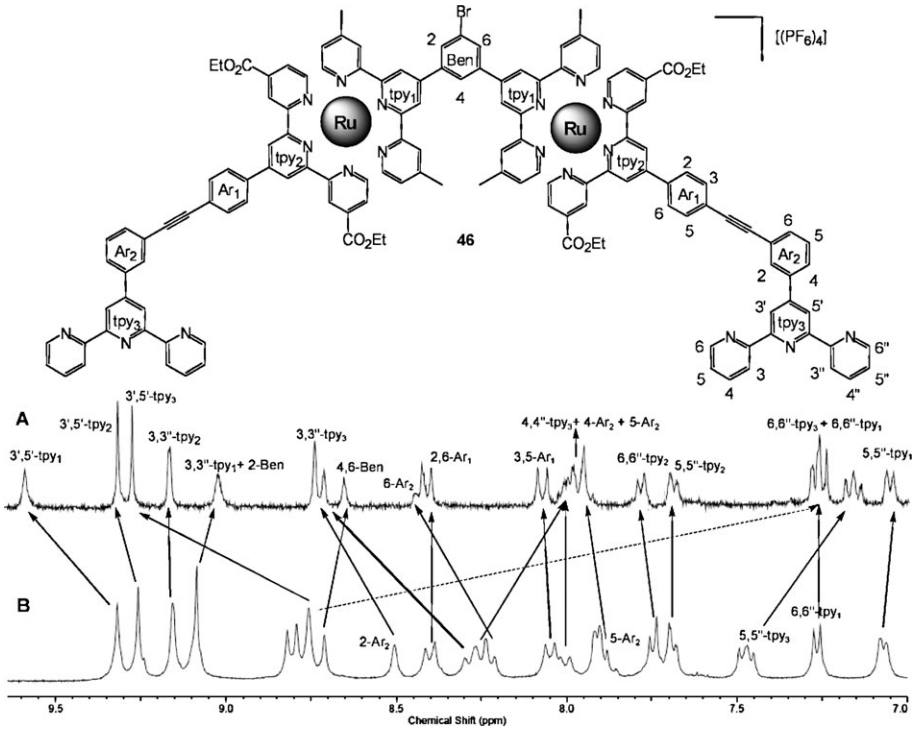


Fig. 7 Aromatic region of ^{1}H NMR (300 MHz) of (A) **47**[$(PF_6)_{12}$] and (B) **46**[$(PF_6)_4$] in CD_3CN at 25 °C.

and matrix assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry.

The crystal structures were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The reflections from three different orientations were used to determine the unit cell. Multi-scan SADABS was used to make corrections. The Bruker SHELXTL computer program was used to solve structures, refine, and model. The structures were obtained by full-matrix least-squares refinement of F^2 and the selection of appropriate atoms from the generated difference map.

Syntheses

3,5-Bis(4,4″-dimethyl-2,2′:6′,2″-terpyridin-4′-yl)-1-bromobenzene, 8. To a stirred solution of **3** (2.02 g, 9.48 mmol) and 2-acetyl-4-methylpyridine (5.31 g, 39.3 mmol) in EtOH (300 mL) at 25 °C, aqueous NaOH (4 M, 10 mL) was added. The mixture was stirred for 9 h at 25 °C, then concentrated *in vacuo* to yield a dark brown diketone intermediate **6**. To a stirred solution of intermediate **6** in AcOH (50 mL), NH_4OAc (30 g, excess) was added and the mixture was refluxed for 11 h. The solution was concentrated *in vacuo* to give a paste, which was neutralized with Na_2CO_3 (1 M) and extracted with $CHCl_3$. The combined extract was dried ($MgSO_4$) and then evaporated *in vacuo* to give a residue that was column chromatographed (basic Al_2O_3) eluting with EtOAc–hexane mixture (1 : 1) to give **8**, as a light yellow solid: 820 mg (13%); mp 317–319 °C. ^{1}H NMR δ 2.54 (s, 12 H, tpyCH_3), 7.20 (d, 4 H, 5,5″-tpy*H*, J = 4.8 Hz), 8.1 (d, 2 H, 2,6-Ben*H*, J = 1.2 Hz), 8.24 (s, 1 H, 4-Ben*H*), 8.5 (s, 4 H, 3,3″-tpy*H*), 8.61 (d, 4 H, 6,6″-tpy*H*, J = 4.8 Hz), 8.74 (s, 4 H, 3′,5′-tpy*H*); ^{13}C NMR δ 21.53, 119.31, 122.31, 123.81, 124.82, 125.12, 130.84, 141.55, 148.23, 148.66, 149.12, 155.86, 156.48; HRMS (calc.): m/z = 675.1850 (675.1866, $[M + H]^+$).

1,3-Bis(4,4″-dimethyl-2,2′:6′,2″-terpyridin-4′-yl)-5-methylbenzene, 9. To a stirred solution of **5** (208 mg, 1.41 mmol) and 2-acetyl-4-methylpyridine (800 mg, 5.91 mmol) in EtOH (50 mL) at 25 °C, aqueous NaOH (1 M, 6 mL) was added. Following the above procedure for **8**, after chromatography, the desired product **9** was isolated as a white solid: 50 mg (6%); mp 258–260 °C. ^{1}H NMR δ 2.54 (s, 12 H, tpyCH_3), 2.56 (s, 3 H, BenCH_3), 7.20 (d, 4 H, 5,5″-tpy*H*, J = 4.5 Hz), 7.8 (s, 2 H, 4,6-Ben*H*), 8.15 (s, 1 H, 2-Ben*H*), 8.52 (s, 4 H, 3,3″-tpy*H*), 8.61 (d, 4 H, 6,6″-tpy*H*, J = 4.8 Hz), 8.78 (s, 4 H, 3′,5′-tpy*H*); ^{13}C NMR δ 21.58, 29.89, 119.6, 122.41, 123.69, 125.03, 129.03, 139.51, 139.62, 148.32, 149.12, 150.44, 156.2, 156.28. *Crystal data* for **9**: $C_{41}H_{34}N_6$, M = 610.74 amu, orthorhombic, *Pbca*, a = 11.800(3), b = 13.208(3), c = 41.505(9) Å, V = 6469(2) Å^3, Z = 8, D_c = 1.254 Mg m^{-3}, μ = 0.075 mm^{-1}, F(000) = 2576, Final R indices (for 4792 reflections) [$I > 2\sigma(I)$] were $R1$ = 0.0725, and $R1$ = 0.0990, $wR2$ = 0.1614 for all 38777 data.

1-(Trimethylsilyl)ethynyl-3-ethynyltoluene, 11. To a stirred solution of **10** (600 mg, 4.28 mmol) in dry THF (30 mL) under N_2 at −78 °C, *n*-BuLi (2.5 M, 1.8 mL, 4.5 mmol) was added dropwise. The solution was stirred at −78 °C for 2 h, and then trimethylsilyl chloride (697 mg, 6.42 mmol) was added quickly. The reaction mixture was warmed to 25 °C and stirred overnight. The solution was concentrated *in vacuo* to give an oily residue that was column chromatographed (SiO_2) eluting with hexane to give **11**, as a colorless oil: 409 mg (45%); ^{1}H NMR δ 0.27 (s, 9 H, $(CH_3)_3$Si), 2.30 (s, 3 H, BenCH_3), 3.05 (s, 1 H, C≡C–*H*), 7.25 (s, 1 H, 4-Ben*H*), 7.27 (s, 1 H, 2-Ben*H*), 7.43

(s, 1 H, 6-Ben*H*); ^{13}C NMR δ 0.11, 21.11, 77.57, 83.09, 94.79, 104.39, 122.39, 123.48, 132.84, 132.95, 133.1, 138.31.

1,3-Bis(2,2′;6′,2″-terpyridinyl-4′-phen-4-ylethynyl)toluene, 14. To a stirred solution of **12** (1.77 g, 4.06 mmol) in THF (50 mL) and NEt_3 (50 mL), **10** (250 mg, 1.78 mmol) was added. The mixture was degassed and back-filled with argon (three times) then $Pd(PPh_3)_4$ (207 mg, 180 μmol, 5% per coupling site) and CuI (27 mg, 150 μmol) were added, then stirred for 12 h at 70 °C. The mixture was filtered and washed with THF (20 mL). The filtrate was concentrated *in vacuo* to give a residue that was column chromatographed (basic Al_2O_3) eluting with $CHCl_3$ to give **14**, as a light yellow solid: 1.14 g (85%); mp 178–179 °C; ^{1}H NMR δ 2.4 (s, 3 H, BenCH_3), 7.36 (dd, 4 H, 5,5″-tpy*H*, J_1 = 4.8 Hz, J_2 = 1.2 Hz), 7.39 (s, 2 H, 2,4-Ben*H*), 7.62 (s, 1 H, 6-Ben*H*), 7.70 (d, 4 H, 3,5-Ar*H*, J = 8.4 Hz), 7.89 (td, 4 H, 4,4″-tpy*H*, J_1 = 7.5 Hz, J_2 = 1.8 Hz), 7.92 (d, 4 H, 2,6-Ar*H*, J = 8.4 Hz), 8.7 (dt, 4 H, 3,3″-tpy*H*, J_1 = 7.8 Hz, J_2 = 0.9 Hz), 8.74 (dd, 4 H, 6,6″-tpy*H*, J_1 = 4.8 Hz, J_2 = 0.9 Hz), 8.77 (s, 4 H, 3′,5′-tpy*H*); ^{13}C NMR δ 21.3, 89.62, 90.43, 118.86, 121.58, 123.55, 124.1, 127.5, 132.14, 132.42, 132.5, 137.1, 138.47, 138.6, 149.36, 149.55, 156.26, 156.35; HRMS (calc.): m/z = 755.2910 (755.2923, $[M + H]^+$).

1,3-Bis[4,4″-di(ethoxycarbonyl)-2,2′;6′,2″-terpyridinyl-4′-phen-4-ylethynyl]toluene, 15. To a stirred solution of diester **13** (643.3 mg, 1.11 mmol) in THF (70 mL) and diisopropylamine (25 mL), **10** (66.6 mg, 475 μmol) was added. The mixture was degassed and back-filled with argon (three times), then $Pd(PPh_3)_4$ (44 mg, 38 μmol, 4% per coupling site) and CuI (5.2 mg, 27 μmol) was added to the flask, then stirred for 12 h at 70 °C. The mixture was filtered and washed with THF (20 mL). The filtrate was concentrated *in vacuo* to give a residue that was column chromatographed (basic Al_2O_3) eluting with $CHCl_3$ to give **15**, as a light yellow solid: 431 mg (87%); mp 314–315 °C; ^{1}H NMR δ 1.51 (t, 12 H, tpy$CO_2CH_2CH_3$, J = 7.2 Hz), 2.4 (s, 3 H, BenCH_3), 4.5 (q, 8 H, tpy$CO_2CH_2CH_3$, J = 7.2 Hz), 7.39 (s, 2 H, 2,4-Ben*H*), 7.62 (s, 1 H, 6-Ben*H*), 7.71 (d, 4 H, 3,5-Ar*H*, J = 8.7 Hz), 7.94 (m, 8 H, 2,6-Ar*H*, 5,5″-tpy*H*), 8.8 (s, 4 H, 3′,5′-tpy*H*), 8.88 (dd, 4 H, 6,6″-tpy*H*, J_1 = 5.1 Hz, J_2 = 0.9 Hz), 9.22 (s, 4 H, 3,3″-tpy*H*); ^{13}C NMR δ 14.46, 21.3, 62.04, 89.55, 90.57, 119.37, 121.01, 123.22, 123.51, 124.31, 127.44, 132.14, 132.48, 138.1, 138.61, 139.12, 149.65, 150.03, 155.7, 157.24, 165.47; HRMS (calc.): m/z = 1043.3726 (1043.3768, $[M + H]^+$).

1-[4,4″-Di(ethoxycarbonyl)-2,2′;6′,2″-terpyridinyl-4′-phen-4-ylethynyl]-3-[(trimethylsilyl)ethynyl]toluene, 16. To a stirred solution of diester **13** (234 mg, 400 μmol) in THF (60 mL) and NEt_3 (60 mL), **11** (85 mg, 400 μmol) was added. The mixture was degassed and back-filled with argon (three times), then $Pd(PPh_3)_4$ (34 mg, 29.4 μmol, 7% per coupling site) and CuI (8 mg, 42 μmol) were added to the flask, then stirred for 12 h at 70 °C. The mixture was filtered and washed with THF (20 mL). The filtrate was concentrated *in vacuo* to give a residue that was column chromatographed (basic Al_2O_3) eluting with $CHCl_3$ to give **16**, as a light yellow solid: 220 mg (83%); mp 247–248 °C; ^{1}H NMR δ 0.26 [s, 9 H, $(CH_3)_3$Si], 1.48 (t, 6 H, tpy$CO_2CH_2CH_3$, J = 7.2 Hz), 2.32 (s, 3 H, BenCH_3), 4.47 (q, 4 H, tpy$CO_2CH_2CH_3$, J = 7.2 Hz), 7.26 (s, 1 H, 4-Ben*H*), 7.31 (s, 1 H, 2-Ben*H*), 7.59 (s, 1 H, 6-Ben*H*), 7.62 (d, 2 H, 3,5-Ar*H*, J = 8.1 Hz), 7.85 (m, 4 H, 2,6-Ar*H*, 5,5″-tpy*H*), 8.68 (s, 2 H, 3′,5′-tpy*H*), 8.8 (d, 2 H, 6,6″-tpy*H*, J_1 = 4.8 Hz), 9.13 (s, 2 H, 3,3″-tpy*H*); ^{13}C NMR δ 0.12, 14.41, 21.17, 61.97, 89.4, 90.48, 94.75, 104.51, 119.16, 120.88, 123.11, 123.28, 123.49, 124.2, 127.29, 132.35, 132.41, 132.46, 132.74, 137.89, 138.37, 138.97, 149.38, 149.94, 155.53, 157.11, 165.37; HRMS (calc.): m/z = 664.2638 (664.2631, $[M + H]^+$).

1-[4,4″-Di(ethoxycarbonyl)-2,2′;6′,2″-terpyridinyl-4′-phen-4-ylethynyl]-3-ethynyltoluene, 17. To a stirred solution of **16** (170 mg, 256 μmol) in THF (20 mL) and EtOH (20 mL), KF (24 mg, 413 μmol) was added then the mixture was stirred for 10 h at 25 °C. Solution was concentrated *in vacuo* to give a residue that was column chromatographed (Al_2O_3) eluting with $CHCl_3$ to give **17**, as a white solid: 139 mg (92%); mp 237–238 °C; ^{1}H NMR δ 1.5 (t, 6 H, tpy$CO_2CH_2CH_3$, J = 7.2 Hz), 2.32 (s, 3 H, BenCH_3), 3.1 (s, 1 H, C≡C–*H*), 4.48 (q, 4 H, tpy$CO_2CH_2CH_3$, J = 7.2 Hz), 7.28 (s, 1 H, 4-Ben*H*), 7.35 (s, 1 H, 2-Ben*H*), 7.5 (s, 1 H, 6-Ben*H*), 7.64 (d, 2 H, 3,5-Ar*H*, J = 8.1 Hz), 7.88 (m, 4 H, 2,6-Ar*H*, 5,5″-tpy*H*), 8.72 (s, 2 H, 3′,5′-tpy*H*), 8.83 (d, 2 H, 6,6″-tpy*H*, J_1 = 4.8 Hz), 9.16 (s, 2 H, 3,3″-tpy*H*); ^{13}C NMR δ 14.43, 21.19, 61.99, 77.68, 83.12, 89.53, 90.33, 119.24, 120.92, 122.51, 123.15, 123.41, 124.15, 127.34, 132.4, 132.5, 132.82, 132.94, 138.02, 138.52, 139.02, 149.46, 149.97, 155.6, 157.15, 165.41; HRMS (calc.): m/z = 592.2233 (592.2236, $[M + H]^+$).

4′-(3-Iodophenyl)-2,2′;6′,2″-terpyridine, 18. To a stirred solution of 3-iodobenzaldehyde (2.54 g, 10.9 mmol) and 2-acetylpyridine (2.98 g, 24.6 mmol) in EtOH (250 mL) at 25 °C, aqueous NaOH (1 M, 22 mL) was added. The mixture was stirred for 9 h at 25 °C then concentrated *in vacuo* to yield a dark brown diketone intermediate. To a stirred solution of this intermediate in AcOH (80 mL), NH_4OAc (13 g, excess) was added and the mixture was refluxed for 11 h. Solution was concentrated *in vacuo* to give a paste, which was neutralized with Na_2CO_3 (1 M) and extracted with $CHCl_3$. Organic layers were combined, dried ($MgSO_4$) and then the solvent was evaporated *in vacuo* to give a residue that was column chromatographed (basic Al_2O_3) eluting with an EtOAc–hexane mixture (1 : 1) to give **18**, as a white solid: 1.6 g (34%); mp 156–158 °C; ^{1}H NMR δ 7.24 (t, 1 H, 5-Ar*H*, J = 8.1 Hz), 7.35 (ddd, 2 H, 5,5″-tpy*H*, J_1 = 7.5 Hz, J_2 = 4.8 Hz, J_3 = 1.2 Hz), 7.77 (ddd, 1 H, 4-Ar*H*, J_1 = 7.8 Hz, J_2 = 1.8 Hz, J_3 = 0.9 Hz), 7.83 (ddd, 1 H, 6-Ar*H*, J_1 = 7.5 Hz, J_2 = 1.5 Hz, J_3 = 0.9 Hz), 7.88 (td, 2 H, 4,4″-tpy*H*, J_1 = 7.5 Hz, J_2 = 1.5 Hz), 8.23 (t, 1 H, 2-Ar*H*, J 1.8 Hz), 8.65 (dt, 2 H, 3,3″-tpy*H*, J_1 = 8.1 Hz, J_2 = 1.2 Hz), 8.68 (s, 2 H, 3′,5′-tpy*H*), 8.73 (ddd, 2 H, 6,6″-tpy*H*, J_1 = 4.8 Hz, J_2 = 1.8 Hz, J_3 = 0.9 Hz); ^{13}C NMR δ 95.04, 118.95, 121.58, 124.15, 126.87, 130.75, 136.27, 137.1, 138.11, 140.92, 148.83, 149.97, 156.2, 156.25; HRMS (calc.): m/z = 458.0122 (458.0130, $[M + Na]^+$).

4′-[3-(Trimethylsilyl)ethynylphenyl]-2,2′;6′,2″-terpyridine, 19. To a stirred solution of **18** (1.53 g, 3.48 mmol) in THF (120 mL) and NEt_3 (90 mL), trimethylsilylacetylene (662 mg, 6.74 mmol) was added. The mixture was degassed and

back-filled with argon (three times) then $Pd(PPh_3)_4$ (238 mg, 206 μmol, 6% per coupling site) and CuI (37.7 mg, 197 μmol) was added to the flask and the mixture was degassed and back-filled with argon (two times) then stirred for 12 h at 70 °C. The mixture was filtered and washed with THF (20 mL). The filtrate was concentrated *in vacuo* to give a residue that was column chromatographed (basic Al_2O_3) eluting with $CHCl_3$ to give **19**, as a white solid: 1.2 g (85%); mp 141–143 °C; ^{1}H NMR δ 0.3 [s, 9 H, $(CH_3)_3Si$], 7.37 (dd, 2 H, 5,5″-tpy*H*, J_1 = 5.7 Hz, J_2 = 1.5 Hz), 7.46 (t, 1 H, 5-Ar*H*, J = 7.8 Hz), 7.55 (d, 1 H, 4-Ar*H*, J = 7.5 Hz), 7.85 (d, 1 H, 6-Ar*H*, J = 7.5 Hz), 7.90 (td, 2 H, 4,4″-tpy*H*, J_1 = 7.8 Hz, J_2 = 1.5 Hz), 8.03 (s, 1 H, 2-Ar*H*), 8.67 (d, 2 H, 3,3″-tpy*H*, J = 8.1 Hz), 8.73 (s, 2 H, 3′,5′-tpy*H*), 8.76 (d, 2 H, 6,6″-tpy*H*, J = 4.8 Hz); ^{13}C NMR δ 0.19, 95.15, 104.82, 119.18, 121.72, 124.18, 127.7, 129.1, 131.01, 132.63, 137.35, 138.76, 149.15, 149.79, 155.99, 156.11; HRMS (calc.): m/z = 428.1563 (428.1559, $[M + Na]^+$).

4′-(3-Ethynylphenyl)-2,2′;6′,2″-terpyridine, 20. To a stirred solution of **19** (420 mg, 1.04 mmol) in THF (30 mL), $(n\text{-}Bu)_4NF{\cdot}3H_2O$ (500 mg, 1.59 mmol) was added, then the mixture was stirred for 6 h at 25 °C. Solution was concentrated *in vacuo* to give a residue that was column chromatographed (Al_2O_3) eluting with $CHCl_3$ to give **20**, as a light yellow solid: 330 mg (95%); mp 173–175 °C; ^{1}H NMR δ 3.16 (s, 1 H, ArC≡C–*H*), 7.37 (dd, 2 H, 5,5″-tpy*H*, J_1 = 5.7 Hz, J_2 = 1.5 Hz), 7.47 (t, 1 H, 5-Ar*H*, J = 7.8 Hz), 7.57 (d, 1 H, 4-Ar*H*, J = 7.8 Hz), 7.88 (m, 3 H, 6-Ar*H*, 4,4″-tpy*H*), 8.05 (s, 1 H, 2-Ar*H*), 8.66 (d, 2 H, 3,3″-tpy*H*, J = 7.8 Hz), 8.72 (s, 2 H, 3′,5′-tpy*H*), 8.74 (d, 2 H, 6,6″-tpy*H*, J = 5.1 Hz); ^{13}C NMR δ 78.04, 83.45, 119.05, 121.61, 123.06, 124.15, 127.98, 129.18, 131.16, 132.73, 137.22, 138.88, 149.22, 149.49, 156.09; HRMS (calc.): m/z = 356.1164 (356.1163, $[M + Na]^+$).

25[(Cl)$_2$]. To a stirred solution of **21** (63.1 mg, 152 μmol) in MeOH (50 mL), $FeCl_2{\cdot}4H_2O$ (15.2 mg, 76 μmol) was added then the mixture was refluxed for 8 h. The solution was concentrated *in vacuo* and dried to give **25**, as a purple solid: 69.6 mg (95%); ^{1}H NMR (CD_3OD) δ 2.46 (s, 12 H, tpyCH_3), 7.03 (d, 4 H, 5,5″-tpy*H*, J = 5.1 Hz), 7.06 (d, 4 H, 6,6″-tpy*H*, J = 5.4 Hz), 7.97 (d, 4 H, 3,5-Ar*H*, J = 8.1 Hz), 8.35 (d, 4 H, 2,6-Ar*H*, J = 8.1 Hz), 8.76 (s, 4 H, 3,3″-tpy*H*), 9.43 (s, 4 H, 3′,5′-tpy*H*); HRMS (calc.): m/z = 444.0342 (444.0347, $[M - 2Cl]^{2+}$).

26[(PF$_6$)$_2$]. To a stirred solution of **22** (79 mg, 196 μmol) in MeOH (50 mL), $FeCl_2{\cdot}4H_2O$ (19.6 mg, 98 μmol) was added, then refluxed for 8 h. The solution was concentrated *in vacuo* to give a deep purple precipitate that was column chromatographed (SiO_2) eluting with MeCN–sat. KNO_3 (aq)–H_2O (7 : 1 : 1) then counterion exchanged by treating with an excess NH_4PF_6 (1 M) then dried to give **26**, as a purple solid: 89 mg (91%); ^{1}H NMR (CD_3CN) δ 2.42 (s, 6 H, tpyCH_3), 6.94 (d, 2 H, 6″-tpy*H*, J = 5.1 Hz), 6.98 (d, 2 H, 6-tpy*H*, J = 5.7 Hz), 7.07 (t, 2 H, 5″-tpy*H*, J = 6.9 Hz), 7.16 (d, 2 H, 5-tpy*H*, J = 5.4 Hz), 7.90 (t, 2 H, 4″-tpy*H*, J = 7.8 Hz), 8.00 (d, 4 H, 3,5-Ar*H*, J = 8.7 Hz), 8.22 (d, 4 H, 2,6-Ar*H*, J = 8.1 Hz), 8.52 (s, 2 H, 3-tpy*H*), 8.59 (d, 2 H, 3″-tpy*H*, J = 8.1 Hz), 9.13 (s, 2 H, 3′-tpy*H*), 9.15 (s, 2 H, 5′-tpy*H*); ^{13}C NMR (CD_3CN) δ 21.12, 122.43, 122.55, 125.46, 126.37, 126.52, 128.84, 129.89, 131.03, 134.14, 137.28, 140.12, 151.03, 153.06, 153.36, 154.14, 159.07, 159.77, 162.1, 162.18; HRMS (calc.): m/z = 430.0191 (430.0190, $[M - 2PF_6]^{2+}$).

27[(Cl)$_2$]. To a stirred solution of **23** (164.3 mg, 397 μmol) in MeOH (60 mL), $FeCl_2{\cdot}4H_2O$ (39.5 mg, 198 μmol) was added then refluxed for 20 h. The solution was concentrated *in vacuo* and dried to give **27**, as a purple solid: 178 mg (94%); ^{1}H NMR (CD_3OD) δ 7.22 (t, 2 H, 5″-tpy*H*, J = 6.0 Hz), 7.3 (d, 2 H, 6″-tpy*H*, J = 5.4 Hz), 7.48 (d, 2 H, 5-tpy*H*, J = 5.1 Hz), 7.53 (d, 2 H, 6-tpy*H*, J = 5.7 Hz), 7.98 (d, 4 H, 3,5-Ar*H*, J = 8.1 Hz), 8.03 (t, 2 H, 4″-tpy*H*, J = 7.8 Hz), 8.33 (d, 4 H, 2,6-Ar*H*, J = 8.4 Hz), 8.86 (d, 2 H, 3″-tpy*H*, J = 7.8 Hz), 9.25 (s, 2 H, 3-tpy*H*), 9.51 (s, 2 H, 5′-tpy*H*), 9.58 (s, 2 H, 3′-tpy*H*); ESI-MS (calc.): m/z = 441.0 (441.0, $[M - 2Cl]^{2+}$); MALDI-TOF (calc.): m/z = 882.342 (881.998, $[M - 2Cl]^{2+}$).

28[(Cl)$_2$]. To a stirred solution of **24** (100.1 mg, 224 μmol) in MeOH (50 mL), $FeCl_2{\cdot}4H_2O$ (22.2 mg, 112 μmol) was added then refluxed for 8 h. The solution was concentrated *in vacuo* and dried to give **28**, as a purple solid: 108 mg (95%); ^{1}H NMR (CD_3OD) δ 3.94 (s, 6 H, tpyCO$_2$CH_3), 7.21 (t, 2 H, 5″-tpy*H*, J = 6.0 Hz), 7.31 (d, 2 H, 6″-tpy*H*, J = 5.1 Hz), 7.52 (d, 2 H, 5-tpy*H*, J = 5.7 Hz), 7.62 (d, 2 H, 6-tpy*H*, J = 5.4 Hz), 7.99 (d, 4 H, 3,5-Ar*H*, J = 8.1 Hz), 8.01 (t, 2 H, 4″-tpy*H*, J = 7.8 Hz), 8.37 (d, 4 H, 2,6-Ar*H*, J = 8.4 Hz), 8.87 (d, 2 H, 3″-tpy*H*, J = 7.8 Hz), 9.29 (s, 2 H, 3-tpy*H*), 9.5 (s, 2 H, 5′-tpy*H*), 9.62 (s, 2 H, 3′-tpy*H*); ESI-MS (calc.): m/z = 473.0 (473.0, $[M - 2Cl]^{2+}$); MALDI-TOF (calc.): m/z = 948.276 (948.018, $[M - 2Cl]^{2+}$), 860.117 (860.038, $[M - 2Cl - 2CO_2]^{2+}$).

31. To a stirred solution of **29** (56 mg, 105 μmol) in EtOH (10 mL) and THF (30 mL), $RuCl_3{\cdot}3H_2O$ (35.9 mg, 137 μmol) was added then refluxed for 15 h. After cooling, the mixture was filtered and washed with EtOH (3 × 50 mL) and THF (3 × 50 mL) to give **31**, as a dark red solid: 62 mg (80%).

32. To a stirred solution of **13** (331 mg, 571 μmol) in EtOH (25 mL) and THF (75 mL), $RuCl_3{\cdot}3H_2O$ (155 mg, 594 μmol) was added then refluxed for 15 h. After cooling, the mixture was filtered and washed with EtOH (3 × 50 mL) and THF (3 × 50 mL) to give **32**, as a dark red solid: 380 mg (85%).

33[(Cl)$_2$]. To a stirred solution of **21** (103 mg, 247 μmol) in MeOH (50 mL), $RuCl_3{\cdot}3H_2O$ (32.6 mg, 124 μmol) and *N*-ethylmorpholine (6 drops) was added then refluxed for 10 h. The solution was concentrated *in vacuo* and dried to give **33**, as a dark red solid: 124 mg (98%); ^{1}H NMR (CD_3OD) δ 2.54 (s, 12 H, tpyCH_3), 7.15 (d, 4 H, 5,5″-tpy*H*, J = 5.4 Hz), 7.35 (d, 4 H, 6,6″-tpy*H*, J = 5.7 Hz), 7.93 (d, 4 H, 3,5-Ar*H*, J = 8.4 Hz), 8.28 (d, 4 H, 2,6-Ar*H*, J = 8.7 Hz), 8.83 (s, 4 H, 3,3″-tpy*H*), 9.28 (s, 4 H, 3′,5′-tpy*H*); HRMS (calc.): m/z = 467.0196 (467.0198, $[M - 2Cl]^{2+}$).

34[(PF$_6$)$_2$]. To a stirred solution of **30** (101.3 mg, 201 μmol) in MeOH (60 mL), $RuCl_3{\cdot}3H_2O$ (26.1 mg, 100 μmol) and *N*-ethylmorpholine (6 drops) was added then the mixture was refluxed for 20 h. The solution was concentrated *in vacuo* to give a red precipitate that was column chromatographed

(SiO_2) eluting with MeCN–sat. KNO_3 (aq)–H_2O (7 : 1 : 1) then counterion exchanged by treating with an excess NH_4PF_6 (1 M) and dried to give **34**, as a dark red solid: 55 mg (40%); ^{1}H NMR (CD_3CN) δ 3.94 (s, 12 H, tpyCO$_2$CH_3), 7.6 (s, 8 H, 5,5″-tpy*H*, 6,6″-tpy*H*), 7.99 (d, 4 H, 3,5-Ar*H*, J = 8.4 Hz), 8.19 (d, 4 H, 2,6-Ar*H*, J = 8.7 Hz), 9.12 (s, 4 H, 3,3″-tpy*H*), 9.21 (s, 4 H, 3′,5′-tpy*H*).

35[(CF$_3$CO$_2$)$_2$]. To a stirred solution of **34**[(PF$_6$)$_2$] (27.6 mg, 19.7 μmol) in DMF (15 mL), NaOH (1 M, 5 mL) was added then the mixture was stirred at 60 °C for 12 h. The solvent was removed and TFA in MeCN was added, then the solution was concentrated *in vacuo* to afford a residue that was washed with H_2O (50 mL) to give **35**, as a dark red solid: 24.4 mg (92%); ^{1}H NMR (CD_3CN + CF_3CO_2D) δ 7.61 (s, 8 H, 5,5″-tpy*H*, 6,6″-tpy*H*), 7.97 (d, 4 H, 3,5-Ar*H*, J = 8.1 Hz), 8.19 (d, 4 H, 2,6-Ar*H*, J = 8.74 Hz), 9.14 (s, 4 H, 3,3″-tpy*H*), 9.22 (s, 4 H, 3′,5′-tpy*H*); MALDI-TOF (calc.): m/z = 1054.200 (1053.936, $[M - 2CF_3CO_2]^{2+}$), 1010.215 (1009.946, $[M - 2CF_3CO_2 - CO_2]^{2+}$), 966.225 (965.956, $[M - 2CF_3CO_2 - 2CO_2]^{2+}$), 922.198 (921.966, $[M - 2CF_3CO_2 - 3CO_2]^{2+}$), 878.251 (877.977, $[M - 2CF_3CO_2 - 4CO_2]^{2+}$).

36[(Cl)$_2$]. To a stirred solution of **31** (35 mg, 47.4 μmol) and **21** (19.7 mg, 47.3 μmol) in EtOH (20 mL), *N*-ethylmorpholine (6 drops) was added then the mixture was refluxed for 10 h. The solution was concentrated *in vacuo* and dried to give **36**, as a dark red solid: 53 mg (99%); ^{1}H NMR (CD_3OD) δ 1.38 (t, 6 H, tpy$_1$CO$_2$CH$_2$CH_3, J = 6.9 Hz), 2.52 (s, 6 H, tpy$_2$CH_3), 4.43 (q, 4 H, tpy$_1$CO$_2$CH_2CH$_3$, J = 6.9 Hz), 7.11 (d, 2 H, 5,5″-tpy$_2$*H*, J = 5.7 Hz), 7.3 (d, 2 H, 6,6″-tpy$_2$*H*, J = 5.7 Hz), 7.74 (dd, 2 H, 5,5″-tpy$_1$*H*, J_1 = 6.0 Hz, J_2 = 1.8 Hz), 7.77 (d, 2 H, 6,6″-tpy$_1$*H*, J = 5.7 Hz), 7.93 (dd, 4 H, 3,5-Ar$_1$*H*, 3,5-Ar$_2$*H*, J_1 = 8.7 Hz, J_2 = 0.9 Hz), 8.28 (m, 4 H, 2,6-Ar$_1$*H*, 2,6-Ar$_2$*H*), 8.82 (s, 2 H, 3,3″-tpy$_2$*H*), 9.29 (s, 4 H, 3′,5′-tpy$_2$*H*, 3,3″-tpy$_1$*H*), 9.43 (s, 2 H, 3′,5′-tpy$_1$*H*); HRMS (calc.): m/z = 524.0260 (524.0261, $[M - 2Cl]^{2+}$).

37[(CF$_3$CO$_2$)$_2$]. To a stirred solution of **36**[(Cl)$_2$] (42 mg, 37.6 μmol) in DMF (15 mL), NaOH (1 M, 5 mL) was added then the mixture was stirred at 60 °C for 12 h. The solvent was removed *in vacuo* and TFA in MeCN was added; the solution was concentrated *in vacuo* to afford a residue that was washed with H_2O (50 mL) to give **37**, as a dark red solid: 46.3 mg (96%); ^{1}H NMR (CD_3CN + CF_3CO_2D) δ 2.46 (s, 6 H, tpy$_2$CH_3), 7.02 (d, 2 H, 5,5″-tpy$_2$*H*, J = 5.7 Hz), 7.18 (d, 2 H, 6,6″-tpy$_2$*H*, J = 5.7 Hz), 7.61 (s, 4 H, 5,5″-tpy$_1$*H*, 6,6″-tpy$_1$*H*), 7.93 (m, 4 H, 3,5-Ar$_1$*H*, 3,5-Ar$_2$*H*), 8.15 (m, 4 H, 2,6-Ar$_1$*H*, 2,6-Ar$_2$*H*), 8.55 (s, 2 H, 3,3″-tpy$_2$*H*), 8.98 (s, 2 H, 3′,5′-tpy$_2$*H*), 9.11 (s, 2 H, 3,3″-tpy$_1$*H*), 9.17 (s, 2 H, 3′,5′-tpy$_1$*H*); MALDI-TOF (calc.): m/z = 994.249 (993.987, $[M - 2CF_3CO_2]^{2+}$), 979.242 (978.972, $[M - 2CF_3CO_2 - CH_3]^{2+}$), 950.265 (949.998, $[M - 2CF_3CO_2 - CO_2]^{2+}$), 935.347 (934.982, $[M - 2CF_3CO_2 - CO_2 - CH_3]^{2+}$), 906.332 (906.008, $[M - 2CF_3CO_2 - 2CO_2]^{2+}$).

38[(PF$_6$)$_2$]. To a stirred solution of **32** (195 mg, 248 μmol) and **13** (144 mg, 249 μmol) in EtOH (20 mL), *N*-ethyl-morpholine (6 drops) was added, then the mixture was refluxed for 20 h. The solution was concentrated *in vacuo* to give a red precipitate that was column chromatographed (SiO_2) eluting with MeCN–sat. KNO_3 (aq)–H_2O (7 : 1 : 1) then counterion exchanged by treating with an excess NH_4PF_6 (1 M) followed by drying to give **38**, as a dark red solid: 210 mg (55%); ^{1}H NMR (CD_3CN) δ 1.36 (t, 12 H, tpyCO$_2$CH$_2$CH$_2$CH_3, J = 6.9 Hz), 4.41 (q, 8 H, tpyCO$_2$CH_2CH$_3$, J = 6.9 Hz), 7.6 (s, 8 H, 5,5″-tpy*H*, 6,6″-tpy*H*), 8.06 (d, 4 H, 3,5-Ar*H*, J = 8.7 Hz), 8.16 (d, 4 H, 2,6-Ar*H*, J = 8.4 Hz), 9.1 (s, 4 H, 3,3″-tpy*H*), 9.2 (s, 4 H, 3′,5′-tpy*H*); HRMS (calc.): m/z = 630.0170 (630.0177, $[M - 2PF_6]^{2+}$). *Crystal data* for **38**: $C_{56}H_{47}F_{12}I_2N_7O_8P_2Ru$; M = 1590.84 amu (the formula weight does not include disordered solvent molecules that were removed from the model; please see Experimental special details in the cif file, ESI‡), orthorhombic, $P2_12_12_1$, a = 14.3505(12), b = 14.4204(12), c = 33.419(3) Å, V = 6915.8(10) Å^3, Z = 4, D_c = 1.528 Mg m^{-3}, μ = 1.250 mm^{-1}, F(000) = 3136, Final R indices (for 16295 reflections) [$I > 2\sigma(I)$] were $R1$ = 0.0467, and $R1$ = 0.0630, $wR2$ = 0.1175 for all 60158 data, Flack parameter = 0.011(15).

39[(CF$_3$CO$_2$)$_2$]. To a stirred solution of **38**[(PF$_6$)$_2$] (75 mg, 48.4 μmol) in DMF (15 mL), NaOH (1 M, 5 mL) was added, then the mixture was stirred at 60 °C for 12 h. The solvent was removed and TFA in MeCN was added; the solution was concentrated *in vacuo* to afford a residue that was washed with H_2O (50 mL) to give **39**, as a dark red solid: 66.1 mg (95%); ^{1}H NMR (CD_3CN + CF_3CO_2D) δ 7.6 (s, 8 H, 5,5″-tpy*H*, 6,6″-tpy*H*), 8.05 (d, 4 H, 3,5-Ar*H*, J = 8.7 Hz), 8.12 (d, 4 H, 2,6-Ar*H*, J = 8.4 Hz), 9.13 (s, 4 H, 3,3″-tpy*H*), 9.21 (s, 4 H, 3′,5′-tpy*H*); MALDI-TOF (calc.): m/z = 1148.197 (1147.910, $[M - 2CF_3CO_2]^{2+}$), 1104.278 (1103.920, $[M - 2CF_3CO_2 - CO_2]^{2+}$), 1060.281 (1059.930, $[M - 2CF_3CO_2 - 2CO_2]^{2+}$), 1016.272 (1015.941, $[M - 2CF_3CO_2 - 3CO_2]^{2+}$), 972.240 (971.951, $[M - 2CF_3CO_2 - 4CO_2]^{2+}$).

40[(PF$_6$)$_4$]. To a stirred solution of **32** (97.9 mg, 62 μmol) and **14** (46.9 mg, 124 μmol) in EtOH (20 mL), *N*-ethylmorpholine (six drops) was added then the mixture was refluxed for 24 h. The solution was concentrated *in vacuo* to give a red precipitate, which was column chromatographed (SiO_2) eluting with MeCN: sat. KNO_3 (aq): H_2O (20 : 1 : 1) then counterion exchanged by treating with an excess NH_4PF_6 (1 M) and dried to give **40**, as dark red solid: 95 mg (57%); ^{1}H NMR (CD_3CN) δ 1.37 (t, 12 H, tpy$_2$CO$_2$CH$_2$CH_3, J = 6.9 Hz), 2.44 (s, 3 H, BenCH_3), 4.39 (q, 8 H, tpy$_2$CO$_2$CH_2CH$_3$, J = 6.9 Hz), 7.21 (t, 4 H, 5,5″-tpy$_1$*H*, J = 6.3 Hz), 7.41 (d, 5 H, 6,6″-tpy$_1$*H*, J = 4.5 Hz), 7.48 (s, 2 H, 2,6-Ben*H*), 7.64 (dd, 4 H, 5,5″-tpy$_2$*H*, J_1 = 5.7 Hz, J_2 = 1.5 Hz), 7.67 (d, 4 H, 6,6″-tpy$_2$*H*, J = 5.7 Hz), 7.97 (m, 12 H, 4,4″-tpy$_1$*H*, 3,5-Ar$_1$*H*, 2,6-Ar$_1$*H*, 6-Ben*H*), 8.14 (d, 4 H, 3,5-Ar$_2$*H*, J = 8.4 Hz), 8.28 (d, 4 H, 2,6-Ar$_2$*H*, J = 8.4 Hz), 8.70 (d, 4 H, 3,3″-tpy$_1$*H*, J = 8.1 Hz), 9.07 (s, 4 H, 3′,5′-tpy$_1$*H*), 9.11 (s, 4 H, 3,3″-tpy$_2$*H*), 9.18 (s, 4 H, 3′,5′-tpy$_2$*H*); HRMS (calc.): m/z = 529.0571 (529.0561, $[M - 4PF_6]^{4+}$).

41[(CF$_3$CO$_2$)$_4$]. To a stirred solution of **40**[(PF$_6$)$_4$] (27 mg, 10 μmol) in DMF (15 mL), NaOH (1 M, 5 mL) was added then the mixture was stirred at 60 °C for 12 h. The solvent was removed *in vacuo* and TFA in MeCN was added; the solution

was concentrated *in vacuo* to afford a residue that was washed with H_2O (50 mL) to give **41**, as a dark red solid: 22 mg (95%); ^{1}H NMR (CD_3CN + CF_3CO_2D) δ 2.46 (s, 3 H, BenCH_3), 7.20 (t, 4 H, 5,5″-tpy$_1$$H$, J = 6.3 Hz), 7.40 (d, 5 H, 6,6″-tpy$_1$$H$, J = 4.5 Hz), 7.53 (s, 2 H, 2,6-Ben$H$), 7.62 (dd, 4 H, 5,5″-tpy$_2$$H$, J_1 = 5.7 Hz, J_2 = 1.5 Hz), 7.66 (d, 4 H, 6,6″-tpy$_2$$H$, J = 5.7 Hz), 7.98 (m, 12 H, 4,4″-tpy$_1$$H$, 3,5-Ar$_1$$H$, 2,6-Ar$_1$$H$, 6-Ben$H$), 8.12 (d, 4 H, 3,5-Ar$_2$$H$, J = 8.4 Hz), 8.27 (d, 4 H, 2,6-Ar$_2$$H$, J = 8.4 Hz), 8.71 (d, 4 H, 3,3″-tpy$_1$$H$, J = 8.1 Hz), 9.07 (s, 4 H, 3′,5′-tpy$_1$$H$), 9.14 (s, 4 H, 3,3″-tpy$_2$$H$), 9.20 (s, 4 H, 3′,5′-tpy$_2$$H$); MALDI-TOF (calc.): m/z = 2003.400 (2003.102, $[M - 4CF_3CO_2]^{4+}$), 1961.422 (1961.113, $[M - 4CF_3CO_2 - CO_2]^{4+}$), 1914.445 (1914.124, $[M - 4CF_3CO_2 - 2CO_2]^{4+}$), 1872.485 (1872.130, $[M - 4CF_3CO_2 - 3CO_2]^{4+}$), 1831.518 (1831.144, $[M - 4CF_3CO_2 - 4CO_2]^{4+}$).

43. To a stirred solution of diester **40**[$(PF_6)_4$] (104 mg, 40 μmol) in a THF (30 mL), MeCN (30 mL) and NEt_3 (50 mL) solvent mixture, **17** (59 mg, 100 μmol) was added. The mixture was degassed and back-filled with argon (three times), then $Pd(PPh_3)_4$ (10.1 mg, 8.7 μmol, 10% per coupling site) and CuI (1.4 mg, 7.3 μmol) were added, then stirred for 12 h at 70 °C. After concentration *in vacuo* and washing with MeCN, the residue was column chromatographed (basic Al_2O_3) eluting with $CHCl_3$ to give **43**, as a yellow solid: 36 mg (64%); mp 275–277 °C; ^{1}H NMR δ 1.51 (t, 12 H, tpyCO$_2$CH$_2$CH_3, J = 6.9 Hz), 2.38 (s, 6 H, BenCH_3), 4.51 (q, 8 H, tpyCO$_2$CH_2CH$_3$, J = 6.9 Hz), 7.35 (s, 2 H, 4-Ben$H$), 7.41 (s, 2 H, 2-Ben$H$), 7.57 (s, 2 H, 6-Ben$H$), 7.71 (d, 4 H, 3,5-ArH, J = 7.8 Hz), 7.94 (m, 8 H, 2,6-ArH, 5,5″-tpy$H$), 8.8 (s, 4 H, 3′,5′-tpy$H$), 8.88 (d, 4 H, 6,6″-tpy$H$, J = 4.8 Hz), 9.23 (s, 4 H, 3,3″-tpy$H$); HRMS (calc.): m/z = 1181.4253 (1181.4238, $[M + H]^+$). The MeCN filtrate was concentrated *in vacuo* to afford a red microcrystalline solid, which is the starting material, dinuclear **40**[$(PF_6)_4$] (95 mg).

44[$(Cl)_4$]. To a stirred solution of **32** (128 mg, 162.6 μmol) and **8** (54.9 mg, 81.3 μmol) in EtOH (80 mL), *N*-ethylmorpholine (six drops) was added, then the mixture was refluxed for 9 h. The solution was concentrated *in vacuo* and dried to give **44**, as a dark red solid: 174 mg (98%); ^{1}H NMR δ 1.4 (t, 12 H, tpy$_2$CO$_2$CH$_2$CH_3, J = 7.2 Hz), 2.58 (s, 12 H, tpy$_1$CH_3), 4.46 (q, 8 H, tpy$_2$CO$_2$CH_2CH$_3$, J = 7.2 Hz), 7.14 (d, 4 H, 5,5″-tpy$_1$$H$, J = 5.4 Hz), 7.33 (d, 4 H, 6,6″-tpy$_1$$H$, J = 5.7 Hz), 7.81 (d, 4 H, 5,5″-tpy$_2$$H$, J = 5.7 Hz), 7.88 (d, 4 H, 6,6″-tpy$_2$$H$, J = 5.7 Hz), 8.15 (s, 8 H, 3,5-ArH, 2,6-ArH), 8.82 (s, 2 H, 2,6-Ben$H$), 9.19 (s, 4 H, 3,3″-tpy$_1$$H$), 9.31 (s, 4 H, 3′,5′-tpy$_2$$H$), 9.46 (s, 5 H, 3,3″-tpy$_2$$H$, 4-Ben$H$), 9.72 (s, 4 H, 3′,5′-tpy$_1$$H$); MALDI-TOF (calc.): m/z = 2190.458 (2190.146, $[M - 4Cl + DHB]^{4+}$), 2143.432 (2143.027, $[M - Cl]^+$), 2036.611 (2036.119, $[M - 4Cl]^{4+}$).

45[$(CF_3CO_2)_4$]. To a stirred solution of **44**[$(PF_6)_4$] (34 mg, 15.6 μmol) in DMF (15 mL), NaOH (1 M, 5 mL) was added then the mixture was stirred at 60 °C for 12 h. The solvent was removed *in vacuo* and a solution of TFA in MeCN was added then the solution was concentrated *in vacuo* to afford a residue that was washed with H_2O (50 mL) to give **45**, as a dark red solid: 30 mg (98%); ^{1}H NMR (CD_3CN + CF_3CO_2D) 2.55 (s, 12 H, tpy$_1$CH_3), 7.17 (d, 4 H, 5,5″-tpy$_1$$H$, J = 5.4 Hz), 7.24 (d, 4 H, 6,6″-tpy$_1$$H$, J = 5.7 Hz), 7.66 (d, 4 H, 5,5″-tpy$_2$$H$, J = 5.7 Hz), 7.67 (d, 4 H, 6,6″-tpy$_2$$H$, J = 5.7 Hz), 8.06 (d, 4 H, 3,5-ArH, J = 8.7 Hz), 8.14 (d, 4 H, 2,6-ArH, J = 8.4 Hz), 8.68 (s, 4 H, 3,3″-tpy$_1$$H$), 72 (s, 2 H, 2,6-Ben$H$), 9.01 (s, 1 H, 4-Ben$H$), 9.14 (s, 4 H, 3′,5′-tpy$_2$$H$), 9.20 (s, 4 H, 3,3″-tpy$_2$$H$), 9.25 (s, 4 H, 3′,5′-tpy$_1$$H$); MALDI-TOF (calc.): m/z = 1924.421 (1923.994, $[M - 4CF_3CO_2]^{4+}$), 1880.342 (1880.004, $[M - 4CF_3CO_2 - CO_2]^{4+}$).

46[$(PF_6)_4$]. To a stirred solution of diester **45**[$(PF_6)_4$] (102 mg, 51 μmol) in DMF (30 mL), and NEt_3 (30 mL), **20** (41 mg, 123 μmol) was added. The mixture was degassed and back-filled with argon (three times) then $Pd(PPh_3)_4$ (9.5 mg, 8.2 μmol, 8% per coupling site) was added to the flask then stirred for 2 days at 70 °C. The mixture was concentrated *in vacuo* to give a red solution that was loaded on a TLC plate (SiO_2) eluting with MeCN–sat. KNO_3 (aq)–H_2O (7 : 1 : 1), the third band (darkest) were removed from the plate and washed with an eluting solvent, followed by counterion exchange by the addition of excess NH_4PF_6 (1 M) to give **46**, as a dark red solid: 55 mg (35%); ^{1}H NMR (CD_3CN) δ 1.38 (t, 12 H, tpy$_2$CO$_2$CH$_2$CH_3, J = 7.2 Hz), 2.52 (s, 12 H, tpy$_1$CH_3), 4.41 (q, 8 H, tpy$_2$CO$_2$CH_2CH$_3$, J = 7.2 Hz), 7.08 (d, 4 H, 5,5″-tpy$_1$$H$, J = 5.1 Hz), 7.27 (d, 4 H, 6,6″-tpy$_1$$H$, J = 5.7 Hz), 7.47 (t, 4 H, 5,5″-tpy$_3$$H$, J = 5.4 Hz), 7.70 (d, 4 H, 5,5″-tpy$_2$$H$, J = 5.7 Hz), 7.74 (d, 4 H, 6,6″-tpy$_2$$H$, J = 6.0 Hz), 7.9 (m, 6 H, 4,4″-tpy$_3$$H$, 5-Ar$_2$$H$), 8.03 (m, 6 H, 3,5-Ar$_1$$H$, 4-Ar$_2$$H$), 8.24 (m, 6 H, 3,3″-tpy$_3$$H$, 6-Ar$_2$$H$), 8.41 (d, 4 H, 2,6-Ar$_1$$H$, J = 8.1 Hz), 8.5 (s, 2 H, 2-Ar$_2$$H$), 8.71 (s, 2H, 2,6-Ben$H$), 8.76 (s, 4 H, 3′,5′-tpy$_3$$H$), 8.6 (d, 4 H, 6,6″-tpy$_3$$H$, J = 8.1 Hz), 9.09 (s, 5 H, 3,3″-tpy$_1$$H$, 4-Ben$H$), 9.16 (s, 4 H, 3′,5′-tpy$_1$$H$), 9.26 (s, 4 H, 3,3″-tpy$_2$$H$), 9.32 (s, 4 H, 3′,5′-tpy$_1$$H$); MALDI-TOF (calc.): m/z = 2736.004 (2736.481, $[M - 2PF_6]^{2+}$), 2593.831 (2593.519, $[M - 3PF_6]^{3+}$).

47[$(PF_6)_{12}$]. To a stirred solution of **46**[$(PF_6)_4$] (5.6 mg, 1.82 μmol) in EtOH (8 mL) and acetone (10 mL), $FeCl_2{\cdot}4H_2O$ (370 μg, 1.83 μmol) was added, then the mixture was refluxed for 8 h. The mixture was concentrated *in vacuo* to give a red solution that was loaded on a TLC plate (SiO_2) eluting with MeCN: sat. KNO_3 (aq): H_2O (7 : 1 : 1), the top band was removed from the plate and washed with an eluting solvent, followed by counterion exchange by the addition of excess NH_4PF_6 (1 M) to afford the hexanuclear **47**[$(PF_6)_{12}$], as a pink solid: 2.4 mg (42%); ^{1}H NMR (CD_3CN) ^{1}H NMR (CD_3CN) δ 1.37 (t, 24 H, tpy$_2$CO$_2$CH$_2$CH_3, J = 7.2 Hz), 2.55 (s, 24 H, tpy$_1$CH_3), 4.43 (q, 16 H, tpy$_2$CO$_2$CH_2CH$_3$, J = 7.2 Hz), 7.06 (d, 8 H, 5,5″-tpy$_1$$H$, J = 6.0 Hz), 7.47 (t, 8 H, 5,5″-tpy$_3$$H$, J = 6.6 Hz), 7.26 (m, 16 H, 6,6″-tpy$_1$$H$, 6,6″-tpy$_3$$H$), 7.70 (d, 8H, 5,5″-tpy$_2$$H$, J = 5.7 Hz), 7.74 (d, 8 H, 6,6″-tpy$_2$$H$, J = 6.0 Hz), 7.98 (m, 16 H, 4,4″-tpy$_3$$H$, 4-Ar$_2$$H$, 5-Ar$_2$$H$), 8.06 (d, 8 H, 3,5-Ar$_1$$H$, J = 8.1 Hz), 8.43 (d, 12 H, 2,6-Ar$_1$$H$, 6-Ar$_2$$H$, J = 8.1 Hz), 8.65 (s, 4 H, 2,6-Ben$H$), 8.74 (d, 12 H, 3,3″-tpy$_3$$H$, 2-Ar$_2$$H$, J = 8.1 Hz), 9.02 (s, 8 H, 3,3″-tpy$_1$$H$), 9.16 (s, 8 H, 3,3″-tpy$_2$$H$), 9.27 (s, 8 H, 3′,5′-tpy$_3$$H$), 9.32 (s, 8 H, 3′,5′-tpy$_2$$H$), 9.59 (s, 8 H, 3′,5′-tpy$_1$$H$). MALDI-TOF (calc.): m/z = 2593.774 (2593.519, $[M - 11PF_6 - 2Fe]^{3+}$), 2466.765

(2466.474, $[M - 11PF_6 - PF_5 - 2Fe]^{4+}$), 2446.552 (2446.256, $[M - 12PF_6 - 2Fe]^{4+}$).

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