Bucky Ligands: Synthesis, Ruthenium(II) Complexes, and Electrochemical Properties

Dominique Armspach, Edwin C. Constable,* François Diederich,* Catherine E. Housecroft,* and Jean-François Nierengarten

Abstract: The novel tridentate 2,2′:6′,2″-terpyridine ligand (**1**) in which the metal-binding domain is directly attached to a methanofullerene C_{60} unit was incorporated into ruthenium-based diads and triads that may undergo photoinduced charge separation. In this paper, the new complexes are compared with more flexible analogues in which the C_{60} fragment is separated from the metal-binding domain by a flexible spacer. Both ^{1}H NMR spectroscopic and cyclic voltammetric studies reveal significant interactions between the fullerene substituent and the metal centre when they are spatially close.

Keywords: heterocycles · fullerenes · ruthenium · supramolecular chemistry

Introduction

As a result of its unusual electrochemical and electronic properties,[1] the fullerene C_{60} is an attractive functional group for molecular electronics[2] and light-harvesting devices.[3] Although initial work was carried out on charge-transfer complexes based on C_{60} itself,[4] recent developments in the functionalisation of fullerenes[5] allow the preparation of covalent C_{60} derivatives bearing electro- and/or photo-active substituents.[6–9] These systems facilitate the study of intramolecular processes between C_{60} and its substituents, which include energy- and electron-transfer interactions. The attachment of fullerenes to metal-binding domains[7–9] that can undergo coordination-initiated assembly into multifunctional systems is of particular interest, and an example of a remote functionalised ruthenium(II) complex has recently been reported.[7c] Such a compound that combines the properties of both C_{60} and the tris(2,2′-bipyridine)ruthenium(II) cation, $[Ru(bpy)_3]^{2+}$, is particularly interesting from both the electrochemical and the photophysical points of view.[7c] As a part of our continuing studies in supramolecular chemistry, some of us have recently incorporated C_{60} in a multicomponent molecular system, namely a copper(I) rotaxane with two fullerene stoppers[9] in which intramolecular photoinduced electron transfer was observed from the ^{3}MLCT state of a bis(diphenyl-1,10-phenanthroline)copper(I) complex to the fullerene.[10] In this paper, we now report the synthesis of various fullerene-substituted oligopyridine ligands, the preparation of the corresponding ruthenium(II) complexes and their electrochemical properties. A preliminary account of this work has recently been reported[8] and we have described the synthesis of diads and triads using ligands **2** and **3** in which the 2,2′:6′,2″-terpyridine (tpy) metal-binding domain is separated from the fullerene by polyethyleneoxy spacers of various lengths. In order to limit the number of back electron-transfer pathways and hopefully increase the lifetime of any photoinduced charge-separated state, we decided to embark on the synthesis of a more rigid fullerene-containing tpy ligand and to investigate its coordination behaviour. Accordingly, we have prepared ligand **1**, in which a methanofullerene unit is directly attached to the metal-binding tpy domain. We also report the synthesis of the soluble 2,2′-bipyridine (bpy) ligand **4** with two fullerene substituents and describe the preparation of the ruthenium(II) complex, $[Ru(bpy)_2(\mathbf{4})][PF_6]_2$.

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Results and Discussion

Preparation of the 2,2′-bipyridine ligand: The synthetic route leading to the fullerene-functionalised bpy ligand **4** is depicted in Scheme 1 and is based on an esterification reaction of 2,2′-

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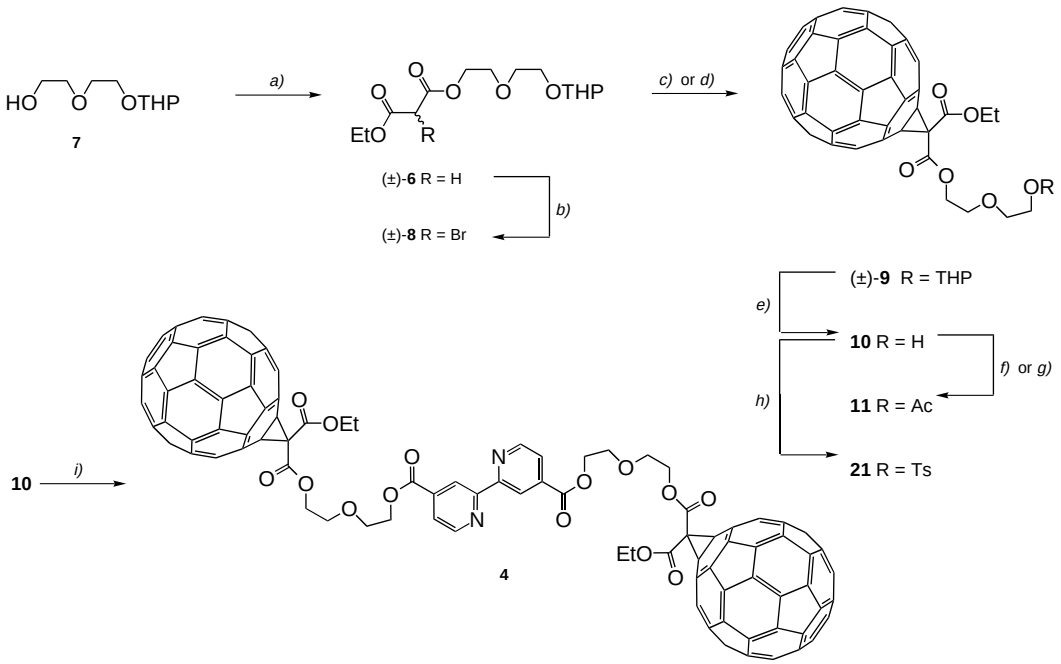

Scheme 1. Synthesis of the bpy ligand **4**: a) EtO_2CCH_2COCl, pyridine, CH_2Cl_2, 0 °C to RT (81 %); b) DBU, THF, 0 °C to RT, then −78 °C, CBr_4 (62 %); c) C_{60}, DBU, toluene, RT (from **8**, 64 %); d) C_{60}, DBU, I_2, toluene, RT (from **6**, 57 %); e) *p*-TsOH, EtOH, toluene, 60 °C (94 %); f) AcOH, DCC, DMAP, CH_2Cl_2, RT (93 %); g) AcCl, Et_3N, CH_2Cl_2, RT (89 %); h) TsCl, pyridine, CH_2Cl_2, −2 °C to RT (69 %); i) **5**, Et_3N, $CHCl_3$, reflux (53 %).

bipyridine-4,4′-dicarbonyl chloride (**5**) with a C_{60} alcohol derivative.

Compound (±)-**6** was prepared in 81 % yield from ethyl malonyl chloride and (±)-2-[2-(3,4,5,6-tetrahydro-*2H*-pyran-2-yloxy)ethoxy]ethanol (**7**)[11] in CH_2Cl_2 at room temperature in the presence of pyridine. Treatment of (±)-**6** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and CBr_4 in THF led to a 62 % yield of the α-bromomalonate derivative (±)-**8** as a mixture of diastereoisomers. The functionalisation of C_{60} is based on the Bingel reaction.[12] Nucleophilic addition of a stabilised α-halocarbanion to the C_{60} core, followed by an intramolecular nucleophilic substitution, leads to clean cyclopropanation of C_{60}.[13] The reaction of C_{60} with compound (±)-**8** in the presence of DBU yielded methanofullerene (±)-**9** in 64 % yield. Compound (±)-**9** could also be prepared directly from precursor (±)-**6**. In this case, the corresponding α-halomalonate derivative is prepared in situ from the reaction of the malonate with iodine,[14–15] and the one-pot reaction of C_{60} with (±)-**6**, iodine and DBU in toluene at room temperature afforded (±)-**9** in 57 % yield. The removal of the 3,4,5,6-tetrahydro-*2H*-pyranyl (THP) group in **9** was carried out by treatment with an excess of 4-toluenesulfonic acid (TsOH) in a mixture of ethanol and toluene at 60 °C for 3 hours. The desired C_{60} alcohol derivative **10** was thereby obtained in 94 % yield. In order to probe the potential of **10** as a building block for the construction of functionalised C_{60} derivatives, different esterification reactions were investigated. The reaction of **10** and acetyl chloride in CH_2Cl_2 in the presence of pyridine gave the corresponding acetate **11** in 89 % yield. Compound **11** could also be prepared in 93 % yield by the *N,N*′-dicyclohexylcarbodiimide (DCC) mediated esterification[16] of **10** with acetic acid.

The preparation of the bis-C_{60}-bpy derivative **4** was initially attempted from alcohol **10** and commercially available 2,2′-bipyridine-4,4′-dicarboxylic acid (**12**) in various solvents (CH_2Cl_2, DMSO and DMF) with DCC as a coupling reagent. In each case no reaction was observed at room temperature, which is probably a consequence of the insolubility of **12**. When the reaction mixture was heated, extensive degradation took place and no further effort was made in order to prepare **4** by this route. In contrast, the reaction of the bis(acid chloride) **5**,[17] which results from the reaction of diacid **12** with thionyl chloride, with alcohol **10** in the presence of triethylamine and refluxed in $CHCl_3$ for 15 hours gave the desired ligand **4** in 53 % yield. Compound **4** with its two C_{60} substituents is soluble in chlorinated organic solvents (CH_2Cl_2 and $CHCl_3$) and complete spectroscopic characterisation was possible. The ^{1}H NMR spectrum of **4** in $CDCl_3$ solution shows three sets of aromatic signals in a typical pattern for a 4,4′-disubstituted bpy,[17] as well as two sets of multiplets corresponding to the ethyleneoxy chains, and a triplet and quartet at $\delta = 1.47$ and 4.68, respectively, for the ethyl groups. The ^{13}C NMR spectrum is also in full agreement with the structure of **4** and 33 resonances out of the 36 expected in the typical fullerene and aromatic region are fully resolved (31 for the fullerene sp^2 carbons and 5 for the bpy moiety) as well as the expected 11 nonaromatic signals ($\delta = 163.36$, 163.60 and 165.06 for the carbonyl groups; $\delta = 71.45$ for the fullerene sp^3 carbons; $\delta = 63.48$, 64.71, 66.01, 68.84 and 69.03 for the OCH_2 groups; $\delta = 52.05$ for the methano bridge carbons; and $\delta = 13.59$ for the CH_3). The composition of ligand **4** was also confirmed by fast atom bombardment (FAB) mass spectroscopy with the molecular ion peak at $m/z = 2086.2$ ($[M^+ + H]$, calculated for $C_{150}H_{33}N_2O_{14}$: 2086.9).

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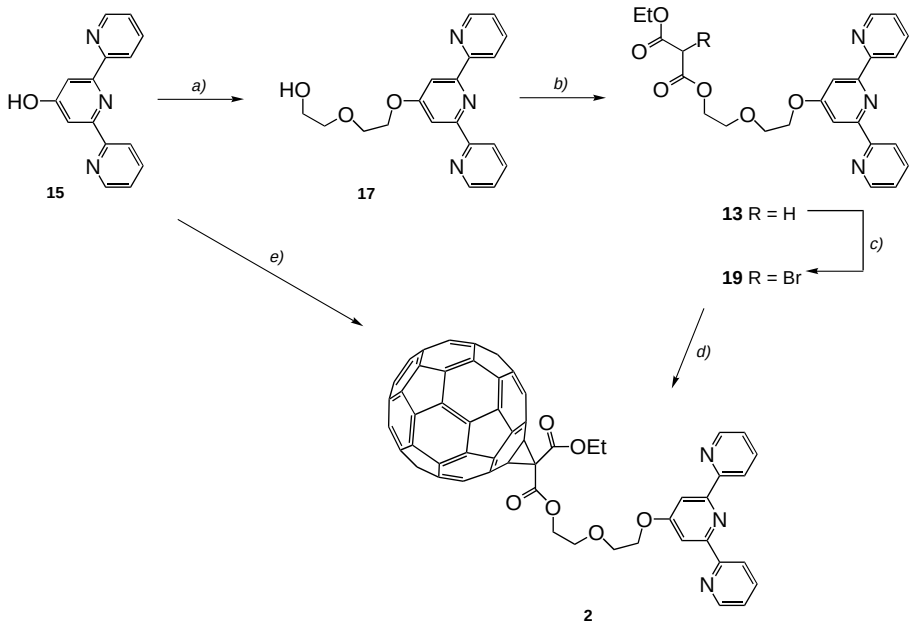
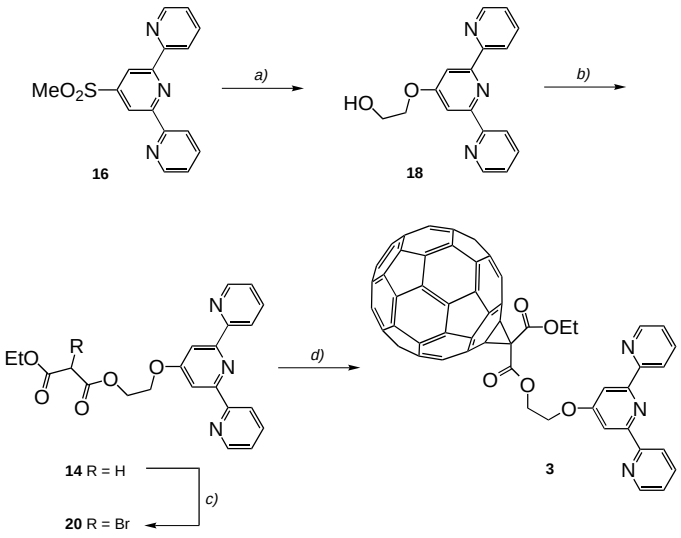
Preparation of the 2,2′:6′,2″-terpyridine ligands: The synthesis of the ligands **2** and **3** in which a tpy metal-binding domain is separated from the methanofullerene moiety by polyethoxy spacers of various lengths is depicted in Schemes 2 and 3.



Scheme 2. Synthesis of the tpy ligand **2**: a) 2-(2-chloroethoxy)ethanol, K_2CO_3, NaI, DMF, 70 °C (82%); b) EtO_2CCH_2COCl, pyridine, CH_2Cl_2, 0 °C to RT (70%); c) DBU, THF, 0 °C to RT, then −78 °C, CBr_4; d) C_{60}, DBU, toluene, RT (52%); e) K_2CO_3, DMF, 60 °C (16%).



Scheme 3. Synthesis of the tpy ligand **3**: a) $FeCl_2$, ethylene glycol, reflux, then H_2O_2, NaOH aq (64%); b) EtO_2CCH_2COCl, pyridine, CH_2Cl_2, 0 °C to RT (70%); c) DBU, THF, 0 °C to RT, then −78 °C, Cbr_4; d) C_{60}, DBU, toluene, RT (55%).

The key malonate derivatives **13** and **14** were prepared in 47 and 57% yields, respectively, in two steps from the known compounds 4′-HOtpy (**15**)[18] and 4′-$MeSO_2$tpy (**16**),[19] respectively. Treatment of **15** with 2-(2-chloroethoxy)ethanol in the presence of an excess of K_2CO_3 and NaI in DMF at 70 °C followed by esterification of the resulting tpy derivative **17** with ethyl malonyl chloride provided the desired intermediate **13**. The metal-activated nucleophilic displacement reaction[20] of the methylsulfonyl group of **16** with ethylene glycol followed by removal of iron by treatment with alkaline hydrogen peroxide led to **18** in 64% yield. Alcohol **18** was treated with ethyl malonyl chloride in the presence of pyridine in CH_2Cl_2 at 0 °C to room temperature to give malonate **14** in 70% yield. The bromination reactions affording **19** and **20** were carried out as follows: **13** or **14**, respectively, was treated with DBU in THF at 20 °C for 30 minutes. The resulting solution was cooled to −78 °C and CBr_4 was added, followed by hydrolysis and work-up. The α-bromomalonate derivatives **19** and **20** thus obtained were used without further purification. Treatment of C_{60} with **19** or **20** under typical Bingel reaction conditions yielded the desired C_{60} functionalised ligands **2** and **3** in good isolated yields (**2**: 52% and **3**: 55%). Compound **2** could also be prepared in two steps from alcohol **10**. Reaction of **10** with 4-toluenesulfonyl chloride (TsCl) in CH_2Cl_2/pyridine 5:1 afforded 4-toluenesulfonate **21** (Scheme 1). Compound **21** was then treated with the tpy derivative **15** (Scheme 2) in DMF in the presence of K_2CO_3 at 60 °C to give ligand **2** only in a modest yield (16%) as a result of partial decomposition of the malonate esters under the basic reaction conditions.[21]

Ligands **2** and **3** were surprisingly soluble in common organic solvents (toluene, CH_2Cl_2, $CHCl_3$) and were readily characterised by conventional spectroscopic methods. The ^{13}C NMR spectra of both **2** and **3** confirmed their C_s symmetry. For each compound, all of the expected nonaromatic signals were observed and a total of 37 resonances out of the 39 expected in the typical aromatic and fullerene region were resolved. In each case, intense molecular ion peaks were observed in the FAB or matrix-assisted laser-desorption time-of-flight (MALDI-TOF) mass spectra of the ligands (Table 1).

The key intermediate in the synthesis of ligand **1**, in which a methanofullerene is directly attached to the metal-binding tpy domain, is 4′-methyl-2,2′:6′,2″-terpyridine (**22**) (Scheme 4). Compound **22** was conveniently prepared using a new general methodology that we have developed[22] from commercially available 3-methylpentanedioic acid (**23**). Diesterification of this acid (methanol, 2,2-dimethoxypropane) followed by treatment of the resulting diester **24** with 2-lithiopyridine (produced in situ from *n*-butyllithium and 2-bromopyridine in the presence of TMEDA) gave the diketone **25** in 41% yield. Cyclisation of **25** with ammonium acetate in acetic acid in the presence of air afforded **22** as a colourless solid in 76%

Table 1. Mass spectrometric data for ligands **1**, **2**, **3**, **4**, **10** and **26**, and their ruthenium complexes.

	Predicted	Observed *m/z*	
	Calcd average mass (exact)[a]	FAB-MS[b]	MALDI-TOF[c]
26	$C_{19}H_{17}N_3O_2$ 319.4 (319.132)	320 $[M^+ + H]$ 247 $[M^+ - CO_2Et + H]$	358 $[M^+ + K]$ 342 $[M^+ + Na]$ 320 $[M^+ + H]$
1	$C_{79}H_{15}N_3O_2$ 1038.0 (1037.116)	1038 $[M^+ + H]$ 966 $[M^+ - CO_2Et + H]$ 720 $[C_{60}^+]$	1039 $[M^+ + H]$ 966 $[M^+ - CO_2Et + H]$
2	$C_{84}H_{23}N_3O_6$ 1170.1 (1169.158)	1170 $[M^+ + H]$ 720 $[C_{60}^+]$	1192 $[M^+ + Na]$ 1170 $[M^+ + H]$
3	$C_{82}H_{19}N_3O_5$ 1126.1 (1125.132)	1126 $[M^+ + H]$ 720 $[C_{60}^+]$	1150 $[M^+ + Na]$ 1127 $[M^+ + H]$ 720 $[C_{60}^+]$
4	$C_{150}H_{32}N_20_{14}$ 2085.9 (2084.185)	2086 $[M^+ + H]$	
$[Ru(\mathbf{26})(tpy)][PF_6]_2$	$C_{34}F_{12}H_{26}N_6O_2P_2Ru$ 941.6 (942.043)		970 $[M^+ + Na]$ 800 $[M^+ - PF_6]$ 655 $[M^+ - 2PF_6]$ 583 $[M^+ - 2PF_6 - CO_2Et]$
$[Ru(\mathbf{1})(tpy)][PF_6]_2$	$C_{94}F_{12}H_{26}N_6O_2P_2Ru$ 1662.3 (1662.043)	1517 $[M^+ - PF_6]$ 1372 $[M^+ - 2PF_6]$ 720 $[C_{60}^+]$	1372 $[M^+ - 2PF_6]$ 1300 $[M^+ - 2PF_6 - CO_2Et]$
$[Ru(\mathbf{2})(tpy)][PF_6]_2$	$C_{99}F_{12}H_{34}N_6O_6P_2Ru$ 1794.4 (1794.086)		1505 $[M^+ - 2PF_6]$ 720 $[C_{60}^+]$
$[Ru(\mathbf{3})(tpy)][PF_6]_2$	$C_{97}F_{12}H_{30}N_6O_5P_2Ru$ 1750.3 (1750.059)		1612 $[M^+ - PF_6]$ 1460 $[M^+ - 2PF_6]$ 720 $[C_{60}^+]$
$[Ru(\mathbf{26})(4'\text{-}Me_2Ntpy)][PF_6]_2$	$C_{36}F_{12}H_{33}N_7O_2P_2Ru$ 986.7 (987.101)		1011 $[M^+ + Na]$ 843 $[M^+ - PF_6]$ 697 $[M^+ - 2PF_6]$ 624 $[M^+ - 2PF_6 - CO_2Et]$
$[Ru(\mathbf{1})(4'\text{-}Me_2Ntpy)][PF_6]_2$	$C_{96}F_{12}H_{31}N_7O_2P_2Ru$ 1705.3 (1705.085)	1560 $[M^+ - PF_6]$ 1414 $[M^+ - 2PF_6]$ 720 $[C_{60}^+]$	1415 $[M^+ - 2PF_6]$ 1343 $[M^+ - 2PF_6 - CO_2Et]$
$[Ru(\mathbf{2})(4'\text{-}Me_2Ntpy)][PF_6]_2$	$C_{101}F_{12}H_{39}N_7O_6P_2Ru$ 1837.5 (1837.128)		1695 $[M^+ - PF_6]$ 1548 $[M^+ - 2PF_6]$ 720 $[C_{60}^+]$
$[Ru(\mathbf{3})(4'\text{-}Me_2Ntpy)][PF_6]_2$	$C_{99}F_{12}H_{35}N_7O_5P_2Ru$ 1793.4 (1793.102)		1649 $[M^+ - PF_6]$ 1502 $[M^+ - 2PF_6]$ 720 $[C_{60}^+]$
$[Ru(\mathbf{4})(bpy)_2][PF_6]_2$	$C_{170}F_{12}H_{52}N_6O_{14}P_2Ru$ 2793.3 (2792.186)	2500 $[M^+ - 2PF_6]$ 1778 $[M^+ - C_{60} - 2PF_6]$ 1251 $[M^{2+} - 2PF_6]$	2639 $[M^+ - PF_6]$ 2492 $[M^+ - 2PF_6]$

[a] Exact masses calculated for all ^{12}C compounds. [b] FAB spectra were recorded using 3-nitrobenzoic acid as matrix. [c] MALDI-TOF spectra were recorded without a matrix or using 2,5-dihydroxybenzoic acid as matrix.

isolated yield. The intermediate dihydropyridine is oxidised by air during the reaction. We consider that the 31% overall yield of **22** in two steps from commercially available starting materials makes this route more convenient than the higher yielding, but longer route previously reported.[23]

Deprotonation of **22** with lithium 2,2,6,6-tetramethylpiperidide,[23] followed by reaction with ethyl chloroformate, gave the monoester **26** in 64% yield together with a small amount of the corresponding diethyl malonate derivative. The desired methanofullerene-substituted ligand **1** was prepared by two different methods. In the first route, the ester **26** was treated with DBU followed by CBr_4 to produce the α-bromoester **27** as a yellow oil which was used without further purification. Cyclopropanation of C_{60} with **27** in toluene with DBU as base gave ligand **1** in a 78% overall yield from **26**. A second and more direct approach involved the one-pot treatment of **26** with I_2, C_{60} and DBU in toluene to give **1** in a moderate yield (26%) in a modification of the Bingel reaction for C_{60} incorporation.[14] All spectroscopic and analytical data for **1** prepared by the two methods are identical and are in full agreement with the proposed formulation. In the mass spectrum of **1**, the expected molecular ion appears as the base peak with additional weaker peaks resulting from the fragmentation of the 4-pyridylacetate unit and ethoxydecarboxylation. The ^{13}C NMR spectrum, in full agreement with the C_s symmetry of **1**, showed the expected 39 resonances in the typical aromatic and fullerene region (31 for the fullerene sp^2 carbons and 8 for the tpy moiety), a signal for the carbonyl group ($\delta = 165.60$), one for the fullerene sp^3 carbons ($\delta = 74.89$), one for the bridgehead carbon ($\delta = 54.70$) and two signals for the ethyl groups ($\delta = 14.30$ and 63.29). The presence of the C_{60} unit has a profound effect on the ^1H

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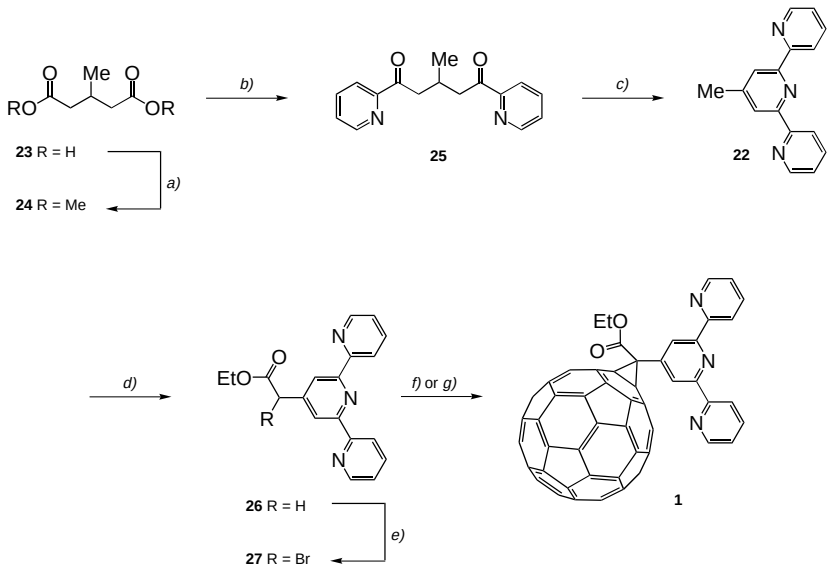
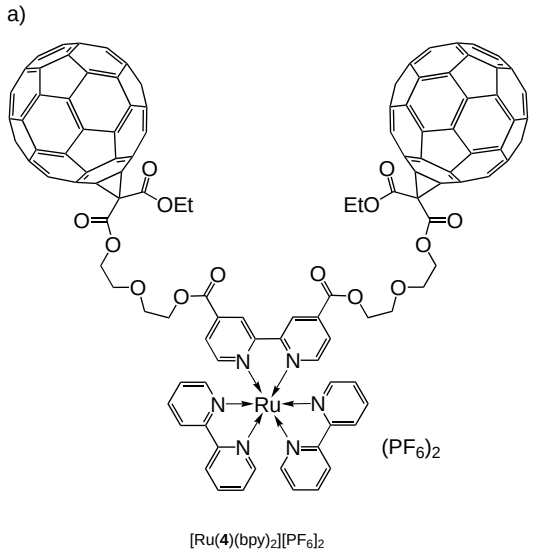
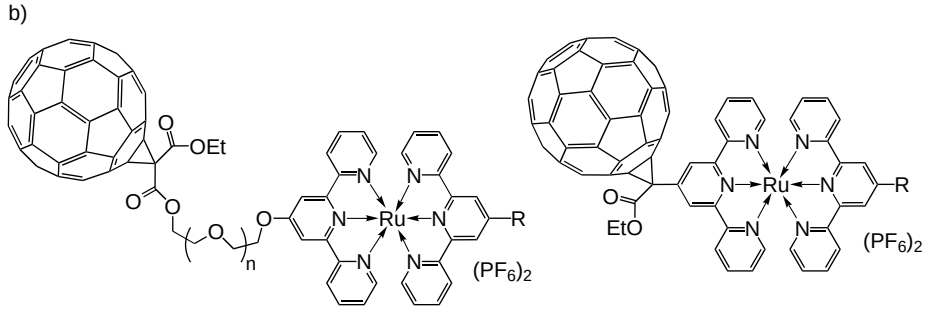


Scheme 4. Synthesis of the tpy ligand **1:** a) 2,2-dimethoxypropane, MeOH, p-TsOH, 45 °C (81 %); b) 2-lithiopyridine, THF, −78 °C (41 %); c) NH_4Ac, AcOH, reflux (76 %); d) lithium 2,2,6,6-tetramethylpiperidide, THF, −10 °C, then $ClCO_2Et$, -10 °C to RT (64 %); e) DBU, THF, 0 °C to RT, then −78 °C, CBr_4; f) C_{60}, DBU, toluene, RT (from **27**, 78 %); g) C_{60}, DBU, I_2, toluene, RT (from **26**, 26 %).



[Ru(**4**)(bpy)$_2$][PF$_6$]$_2$



[Ru(**2**)(tpy)][PF6]$_2$ R = H, n = 1

[Ru(**2**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ R = NMe$_2$, n = 1

[Ru(**3**)(tpy)][PF$_6$]$_2$ R = H, n = 0

[Ru(**3**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ R = NMe$_2$, n = 0

[Ru(**1**)(tpy)][PF$_6$]$_2$ R = H

[Ru(**1**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ R = NMe$_2$

Figure 1. a) Ruthenium(II) complex of the bpy ligand **4**. b) Ruthenium(II) complexes of the tpy ligands **1**–**3**.

NMR spectroscopic resonances of the tpy unit. The H$^{3',5'}$ resonance of the central pyridine ring is shifted strongly downfield with respect to the intermediate **26** (^{1}H NMR $\Delta\delta$ (**1** − **26**) = +0.83) and also with respect to compounds **2** and **3** (^{1}H NMR $\Delta\delta$ (**1** − **2**) = + 1.18). This effect can be ascribed to deshielding by the paramagnetic ring currents of nearby pentagons in the spatially close C_{60} moiety. We noted abnormally low integration values for the H$^{3',5'}$ signal, and T_1 relaxation measurements show that all of the pyridine protons have T_1 values between 0.7 and 2 s with the exception of H$^{3',5'}$ which has a T_1 value of 10 s.

Ruthenium(II) complexes: In order to probe the interactions of the fullerene substituent with electron donors we decided to prepare the diads [Ru(**1**)(tpy)][PF$_6$]$_2$, [Ru(**2**)(tpy)][PF$_6$]$_2$, [Ru(**3**)(tpy)][PF$_6$]$_2$ and [Ru(**4**)(bpy)$_2$][PF$_6$]$_2$ as well as the triads [Ru(**1**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$, [Ru(**2**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ and [Ru(**3**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ (Figure 1) (4′-Me$_2$Ntpy = 4′-dimethylamino-2,2′:6′,2″-terpyridine[26]).

In the triads, the 4′-Me$_2$Ntpy ligand is expected to act as an electron donor. With the exception of [Ru(**4**)(bpy)$_2$][PF$_6$]$_2$, which was prepared by reacting **4** with [Ru(bpy)$_2$Cl$_2$], all complexes were obtained in reasonable yields (22–73 %) from the reaction of **1**, **2** or **3** with either [Ru(tpy)Cl$_3$] or [Ru(4′-Me$_2$Ntpy)Cl$_3$] according to the general procedure reported previously[3d–f]. The mass spectrometric (FAB-MS and MALDI-TOF), ^{1}H and ^{13}C NMR spectroscopic data all confirmed the formation of the desired heteroleptic complexes. Unlike their malonate-based counterparts, both [Ru(**1**)tpy][PF$_6$]$_2$ and [Ru(**1**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ exhibit peaks arising from ethoxydecarboxylation as well as cleavage of the 4-pyridylacetate unit in their mass spectra (Table 1). Additional peaks in the mass spectra result from the successive loss of one and two PF_6 counterions. As noted in the ^{1}H NMR spectrum of the free ligand **1**, there is a marked downfield shift of the H$^{3',5'}$ protons ($\Delta\delta$ ([Ru(**1**)(tpy)][PF$_6$]$_2$ − [Ru(**26**)(tpy)][PF$_6$]$_2$) = +0.81). However, in contrast to the free ligand **1**, the T_1 values for all of protons in the complexes lie within the range 0.6 to 1.7 s. This observation strongly suggests that a metal component could be involved in the relaxation process of H$^{3',5'}$.

Electrochemical and UV/Vis studies: The first fullerene-centred reduction for all complexes occurs to less negative potential than in the correspond-

ing free ligands, and anodic shifts ranging from 30 to 80 mV are observed (Table 2). Conversely, the ruthenium(II)/(III) oxidation potentials in $[Ru(\mathbf{1})(tpy)][PF_6]_2$ and $[Ru(\mathbf{1})(4'\text{-}Me_2Ntpy)][PF_6]_2$ are found to more positive values than in

Table 2. Half-wave potentials[a] of the C_{60}-containing ligands and complexes by cyclic voltammetry.

	C_{60}-centred reductions			Ru^{II}/Ru^{III}
	*E*1	*E*2	*E*3	
19	−1.09	−1.47	−1.90	
1	−1.05	−1.41	−1.92	
2	−1.08	−1.46	−1.91	
3	−1.11	−1.50	−1.90	
4	−1.04	−1.42	−1.93	
$[Ru(4'\text{-EtOtpy})(tpy)][PF_6]_2$[26]				+0.83[b]
$[Ru(\mathbf{26})(tpy)][PF_6]_2$				+0.90
$[Ru(\mathbf{1})(tpy)][PF_6]_2$	−1.00	−1.40	−1.83	+0.95
$[Ru(\mathbf{2})(tpy)][PF_6]_2$	−1.02	−1.43	−1.91	+0.80
$[Ru(\mathbf{3})(tpy)][PF_6]_2$	−1.03	−1.42	−1.80	+0.82
$[Ru(4'\text{-EtOtpy})(4'\text{-}Me_2Ntpy)][PF_6]_2$[26]				+0.52[b]
$[Ru(\mathbf{26})(4'\text{-}Me_2Ntpy)][PF_6]_2$[				+0.56
$[Ru(\mathbf{1})(4'\text{-}Me_2Ntpy)][PF_6]_2$	−1.02	−1.42	−2.01	+0.60
$Ru(\mathbf{2})(4'\text{-}Me_2Ntpy)][PF_6]_2$	−1.01	−1.40	−1.90	+0.48
$[Ru(\mathbf{3})(4'\text{-}Me_2Ntpy)][PF_6]_2$	−0.99	−1.43	−1.82	+0.48
$[Ru(4,4'\text{-}CO_2Etbpy)(bpy)_2][PF_6]_2$[24]				+0.88[c]
$[Ru(\mathbf{4})(bpy)_2][PF_6]_2$	−1.10	−1.48	−1.92	+0.93

[a] V vs. ferrocene/ferrocenium couple; $(n\text{Bu})_4NPF_6$ (0.1M) in CH_2Cl_2; scan rate = 0.1 $V\,s^{-1}$. [b] Recorded in MeCN. [c] Recorded in DMF.

model compounds ($\Delta E_{1/2} = 50$ and 40 mV vs. $[Ru(\mathbf{26})(tpy)][PF_6]_2$ and $[Ru(\mathbf{26})(4'\text{-}Me_2Ntpy)][PF_6]_2$, respectively, Figure 2), whereas those for the complexes containing ethyleneoxy linkers remain practically unchanged. Only a few fullerene-containing metal complexes exhibiting significant anodic shifts have been thus far described.[9] The results we report are in contrast to some other reported examples[7e, 7f] and indicate that there is a degree of interaction between the methanofullerene unit and the metal centre when they are constrained to be spatially close. Although these observations (more facile ligand reduction, harder metal-centred oxidation) appear to be incompatible, we have commented earlier upon the dangers of over facile interpretation of such electrochemical data for ruthenium oligopyridine complexes. In particular, we have shown that the observed potentials are a subtle balance between the stabilisation of metal(II) and metal(III) states by competing π-acceptor and donor properties.[28] In this respect, differential solvation effects produced by the lipophilic C_{60} units may also play an important role.

The electronic absorption spectra of both the diads and triads display absorptions assigned to the ruthenium-tpy subunits and the fullerene moieties. Except for one broad, long-wavelength fullerene-centred band, which is masked by the metal-to-ligand charge transfer (MLCT) absorption, all fullerene-centered diagnostic bands are observed in all complexes at the same wavelengths as in the free ligands (Figure 3). In all cases, these data suggest the absence of charge transfer from the amine substituent of the 4′-Me_2Ntpy ligands to the fullerene in the ground state.

The luminescence properties of both rigid and flexible fullerene-functionalised complexes are currently under investigation in collaboration with the group of Professor Vincenzo Balzani (Bologna). Special emphasis is placed on the detection of photo-induced and long-lived charge-separated states.

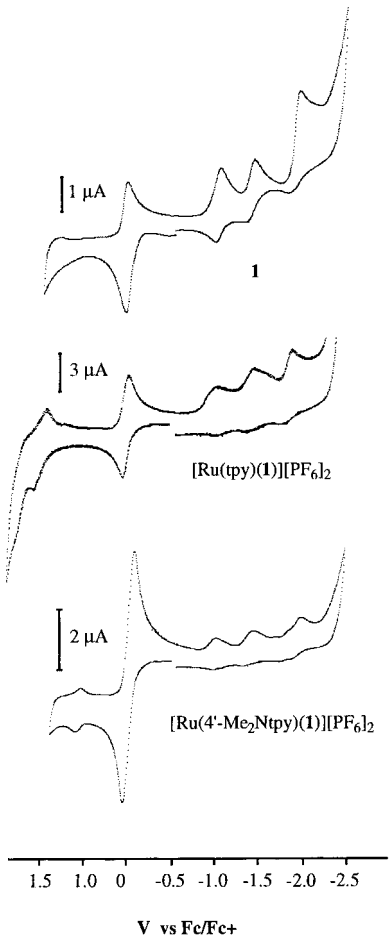


Figure 2. Cyclic voltammograms of **1**, $[Ru(tpy)(\mathbf{1})][PF_6]_2$ and $[Ru(4'\text{-}Me_2Ntpy)(\mathbf{1})][PF_6]_2$ at 0.1 $V\,s^{-1}$ in CH_2Cl_2 containing 0.1M $[n\text{Bu}_4N][PF_6]$.

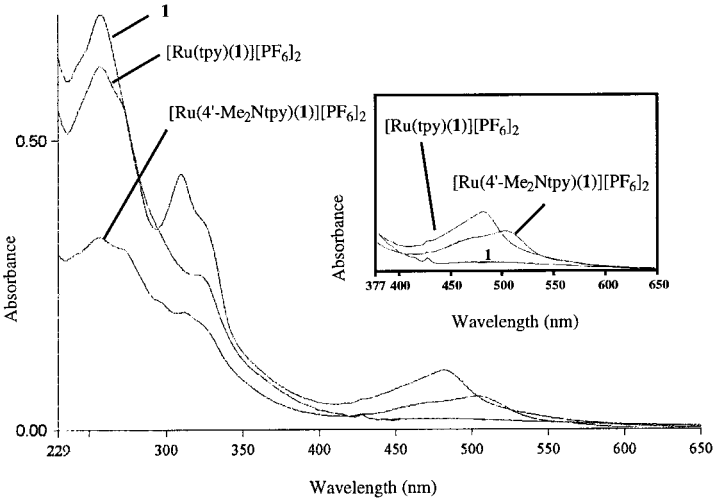


Figure 3. UV and visible absorption spectra of the fullerene compounds in CH_2Cl_2. Concentrations (main panel/inset): **1** (5.9×10^{-6}M/7.4×10^{-5}M), $[Ru(tpy)(\mathbf{1})][PF_6]_2$ (4.8×10^{-6}M/4.8×10^{-5}M), $[Ru(4'\text{-}Me_2Ntpy)(\mathbf{1})][PF_6]_2$ (2.2×10^{-6}M/3.2×10^{-5}M).

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Conclusions

A series of fullerene-functionalised oligopyridine ligands have been prepared and their coordination behaviour investigated. Significant interactions between C_{60} and a directly linked tpy residue have been detected.

Experimental Section

General: Reagents and solvents were generally purchased as reagent grade and used without further purification. Toluene and THF were distilled over sodium benzophenone ketyl. Ethylene glycol was dried over molecular sieves (4 Å). C_{60} was isolated from the commercially available C_{60}/C_{70} mixture according to a previously reported method.[25] (±)-2-[2-(3,4,5,6-Tetrahydro-*2H*-pyran-2-yloxy)ethoxy]ethanol (±)-(**7**),[11] 4′-hydroxy-2,2′:6′,2″-terpyridine (**15**),[18] 4′-methylsulfonyl-2,2′:6′,2″-terpyridine (**16**),[19] 2,2′-bipyridine-4,4′-dicarbonyl chloride (**5**),[17] [Ru(tpy)Cl_3][26] and [Ru(4′-Me_2Ntpy)Cl_3][26] were prepared as previously reported. Evaporation and concentration in vacuo were done at water aspirator pressure; products were dried in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from Merck. Thin-layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from Merck, visualised by UV light. Melting points were measured on a Büchi apparatus and are uncorrected. UV/Vis Spectra were measured on a Varian Cary-5 spectrophotometer or on a Perkin–Elmer Lamda 9 spectrophotometer. IR spectra were measured on Perkin–Elmer 580 or Genesis Series FTIR spectrometers. NMR spectra were recorded on Bruker AM500, AM250 or Varian Gemini300 or 200 spectrometers at 296 or 300 K, with solvent peaks as internal reference. Mass spectra were recorded on a VG Tribrid instrument for EI, a VG ZAB 2SEQ instrument with 4-nitrobenzyl alcohol as matrix for FAB or a PerSeptive Biosystems Vestec spectrometer in positive linear mode at 5 kV acceleration voltage either without a matrix or with 2,5-dihydroxybenzoic acid as matrix for MALDI-TOF. Elemental analyses were performed by the Ciba Forschungsdienste Zentrale Analytik, Basel, or by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich. Electrochemical measurements were performed with an EcoChemie Autolab PGSTAT 20 potentiostat. A conventional three-electrode configuration was used, with glassy carbon working and platinum bead auxiliary electrodes and Ag/AgCl reference. For the electrochemical measurements CH_2Cl_2, freshly distilled from P_4O_{10}, was used as a solvent. The base electrolyte was 0.1M [nBu$_4$N][PF_6], recrystallised twice from ethanol/water and thoroughly dried in vacuo over P_4O_{10}. Potentials are quoted vs. the ferrocene/ferrocenium couple ($Fc/Fc^+ = 0.0$ V), and all potentials were referenced to internal ferrocene added at the end of each experiment.

(±)-2-[2-(3,4,5,6-Tetrahydro-2*H*-pyran-2-yloxy)ethoxy]ethyl ethyl malonate (±)-(**6**): Ethyl malonyl chloride (2.8 mL, 21.98 mmol) was added to a stirred solution of **7** (3.80 g, 19.98 mmol) and pyridine (3.2 mL, 39.96 mmol) in CH_2Cl_2 (300 mL) at 0 °C. The solution was warmed slowly to RT (over 1 h) and stirred for 10 h. The resulting CH_2Cl_2 solution was washed twice with brine, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/4% MeOH) yielded 4.91 g (16.11 mmol, 81%) of **6**. Colourless oil; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.19$ (t, $J = 7.2$ Hz, 3H), 1.30–1.80 (m, 6H), 3.31 (s, 2H), 3.35–3.85 (m, 8H), 4.11 (q, $J = 7.2$ Hz, 2H), 4.22 (m, 2H), 4.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 13.89$, 19.10, 25.06, 30.19, 41.09, 61.10, 61.79, 64.21, 66.25, 68.46, 70.10, 98.55, 166.02, 166.20; IR (neat): $\tilde{\nu} = 1737$ cm^{-1} (C=O); MS (EI): m/z (%) = 303 (0.1) [$M^+ - $H], 275 (0.5) [$M^+ - $Et], 259 (0.2) [$M^+ - $OEt], 159 (2) [THPO(CH$_2$)$_2OCH_2^+$], 115 (14) [THPOCH$_2^+$], 85 (100) [THP$^+$]; $C_{14}H_{24}O_7$ (304.3): calcd C 55.25, H 7.95; found C 55.25, H 7.90.

(±)-2-[2-(3,4,5,6-Tetrahydro-2*H*-pyran-2-yloxy)ethoxy]ethyl ethyl 2-bromomalonate (±)-(**8**): DBU (0.9 mL, 5.92 mmol) was added under N_2 to a stirred solution of (±)-**6** (1.80 g, 5.915 mmol) in dry THF (200 mL) at 0 °C. The resulting solution was warmed slowly to RT (over 30 min), then cooled to −78 °C. CBr_4 (1.96 g, 5.915 mmol) was added and the resulting mixture was stirred under N_2 at −78 °C for 2 h. Saturated aq NH_4Cl (30 mL) was added. The THF solution was diluted with hexane, extracted twice with brine, and the combined aqueous layers were subsequently extracted with CH_2Cl_2. The organic layers were dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/1.5% MeOH) yielded 1.41 g (3.68 mmol, 62%) of (±)-**8**. Colourless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 1.27$ (t, $J = 7.1$ Hz, 3H), 1.40–1.90 (m, 6H), 3.40–3.90 (m, 8H), 4.24 (q, $J = 7.1$ Hz, 2H), 4.33 (m, 2H), 4.58 (m, 1H) 4.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 13.55$, 19.17, 25.09, 30.24, 41.87, 61.92, 62.93, 65.87, 66.32, 68.23, 70.33, 98.64, 164.12, 164.29; IR (neat): $\tilde{\nu} = 1765$, 1743 cm^{-1} (C=O); MS (EI): m/z (%) = 383 (0.2) [M^+], 189 (6) [THPO(CH$_2$)$_2$O(CH$_2$)$_2$O$^+$], 159 (6) [THPO(CH$_2$)$_2$OCH$_2^+$], 115 (7) [THPOCH$_2^+$], 85 (100) [THP$^+$]; $C_{14}H_{23}BrO_7$ (383.2): calcd C 43.88, H 6.05; found C 43.93, H 5.96.

(±)-2-[2-(3,4,5,6-Tetrahydro-2*H*-pyran-2-yloxy)ethoxy]ethyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (±)-(**9**)

Method 1: DBU (0.2 mL, 1.39 mmol) was added under N_2 at RT to a stirred solution of C_{60} (500 mg, 0.694 mmol) and (±)-**8** (266 mg, 0.694 mmol) in toluene (600 mL). The resulting solution was stirred under N_2 at RT for 4 h. The reaction mixture was then filtered over a short plug of silica (toluene then CH_2Cl_2/5% MeOH) and the solvent evaporated. Column chromatography (SiO_2, CH_2Cl_2/0.5% MeOH) followed by recrystallisation from pentane/CH_2Cl_2 yielded 456 mg (0.446 mmol, 64%) of pure (±)-**9**. Dark red solid; m.p. > 280 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.49$ (t, $J = 7.1$ Hz, 3H), 1.50–1.90 (m, 6H), 3.45–3.95 (m, 8H), 4.57 (q, $J = 7$ Hz, 2H), 4.65 (m, 3H); IR (KBr): $\tilde{\nu} = 1745$ cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (120330), 326 (36960), 392 (sh, 4130), 402 (sh, 2830), 413 (sh, 2060), 426 (2130), 490 (1260), 688 nm (155); MS (FAB): m/z (%) = 1022 (3) [M^+], 720 (62) [C_{60}^+], 85 (100) [THP$^+$]; $C_{74}H_{22}O_7 \cdot 0.2\,CH_2Cl_2$ (1040.0): calcd C 85.70, H 2.17; found C 85.84, H 2.21.

Method 2: DBU (0.2 mL, 1.39 mmol) was added under N_2 at RT to a stirred solution of C_{60} (500 mg, 0.694 mmol), iodine (176 mg, 0.694 mmol) and (±)-**6** (266 mg, 0.694 mmol) in toluene (600 mL). The resulting solution was stirred under N_2 at RT for 4 h. The reaction mixture was then filtered over a short plug of silica (toluene then CH_2Cl_2/5% MeOH) and the solvent evaporated. Column chromatography (SiO_2, CH_2Cl_2/0.5% MeOH) followed by recrystallisation from pentane/CH_2Cl_2 yielded 403 mg (0.394 mmol, 57%) of pure (±)-**9**.

2-(2-Hydroxyethoxy)ethyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (**10**): A mixture of (±)-**9** (440 mg, 0.43 mmol) and *p*-TsOH (409 mg, 2.15 mmol) in EtOH/toluene 3:1 (400 mL) was stirred at 60 °C under N_2 for 3 h. The resulting solution was then evaporated to dryness, and column chromatography (SiO_2, CH_2Cl_2/2% MeOH) followed by recrystallisation from pentane/CH_2Cl_2 yielded 381 mg (0.406 mmol, 94%) of pure **10**. Dark red solid; m.p. > 280 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.50$ (t, $J = 7.1$ Hz, 3H), 2.08 (t, $J = 5.9$ Hz, 1H), 3.66 (m, 2H), 3.75 (m, 2H), 3.90 (m, 2H), 4.58 (q, $J = 7.1$ Hz, 2H), 4.68 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 14.21$, 52.09, 61.81, 63.56, 65.98, 68.71, 71.47, 72.40, 138.89, 139.13, 140.95, 140.96, 141.84, 141.87, 142.18, 142.20, 142.96, 143.00, 143.01, 143.07, 143.09, 143.88, 144.59, 144.63, 144.68, 144.89, 145.12, 145.15, 145.17, 145.18, 145.26, 163.56, 163.63; IR (KBr): $\tilde{\nu} = 3423$ (O—H), 1744 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (105500), 327 (31750), 393 (sh, 3460), 402 (sh, 2550), 413 (sh, 1930), 426 (1790), 488 (1290), 688 nm (180); MS (FAB): m/z (%) = 938 (23) [M^+], 720 (100) [C_{60}^+]; $C_{69}H_{14}O_6 \cdot 1/3\,CH_2Cl_2$ (967.2): calcd C 86.10, H 1.53; found C 86.06, H 1.72.

2-[2-(Acetyloxy)ethoxy]ethyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (**11**)

Method 1: A solution of **10** (80 mg, 0.085 mmol), AcOH (5.6 mg, 0.093 mmol), DCC (21 mg, 0.102mmol) and DMAP (5 mg, 0.041 mmol) in CH_2Cl_2 (15 mL) was stirred at RT for 16 h. The resulting dark red mixture was evaporated to dryness, and column chromatography (SiO_2, CH_2Cl_2) followed by recrystallisation from pentane/CH_2Cl_2 yielded 78 mg (0.080 mmol, 93%) of pure **11**. Dark red solid; m.p. > 280 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.49$ (t, $J = 7.1$ Hz, 3H), 2.09 (s, 3H), 3.74 (t, $J = 5.0$ Hz, 2H), 3.88 (t, $J = 5.0$ Hz, 2H), 4.23 (t, $J = 5.0$ Hz, 2H), 4.57 (q, $J = 7.1$ Hz, 2H), 4.66 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 14.22$, 20.95, 52.05, 63.44, 63.47, 65.98, 68.71, 69.20, 71.48, 138.90, 139.16, 140.92, 140.95, 141.84, 141.88, 142.18, 142.20, 142.37, 142.80, 142.95, 142.99, 143.01, 143.07, 143.09, 143.87, 143.88, 144.44, 144.58, 144.61, 144.64, 144.67, 144.68, 144.88, 145.13, 145.14, 145.17, 145.18, 145.26, 145.28, 163.39, 163.60, 170.92; IR (KBr): $\tilde{\nu} = 1741$ cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (104250), 326 (31100), 393 (sh, 3620), 402 (sh, 2500), 413 (sh, 1790), 426 (1870), 490

(1070), 687 nm (110); MS (FAB): m/z (%) = 980 (35) [M^+], 720 (100) [C_{60}^+]; $C_{71}H_{16}O_7 \cdot 0.2\,CH_2Cl_2$ (997.9): calcd C 85.70, H 1.66; found C 85.94, H 1.85.

Method 2: A solution of **10** (50 mg, 0.053 mmol), acetyl chloride (5 mg, 0.064 mmol) and Et_3N (0.1 mL) in dry CH_2Cl_2 (50 mL) was stirred at RT under N_2 for 8 h. The resulting dark red mixture was evaporated to dryness, and column chromatography (SiO_2, CH_2Cl_2) followed by recrystallisation from pentane/CH_2Cl_2 yielded 46 mg (0.047 mmol, 89%) of pure **11**.

Bis{[(61-ethoxycarbonyl)methano[60]fullerene-61-yl]-2-(2-carboxyethoxy)ethyl} 2,2′-bipyridine-4,4′-dicarboxylate (**4**): A solution of **5** (18.4 mg, 0.074 mmol), **10** (153 mg, 0.163 mmol) and Et_3N (0.05 mL) in dry $CHCl_3$ (100 mL) was refluxed under N_2 for 15 h. The resulting dark red mixture was evaporated to dryness, and column chromatography (SiO_2, CH_2Cl_2/1.5 to 2% MeOH) followed by recrystallisation from pentane/CH_2Cl_2 yielded 82 mg (0.039 mmol, 53%) of pure **4**. Dark red solid; m.p. > 280 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.47 (t, J = 7.1 Hz, 6H), 3.92 (m, 8H), 4.54 (m, 4H), 4.55 (q, J = 7.1 Hz, 4H), 4.68 (m, 4H), 7.91 (dd, J = 5.1, 1.5 Hz, 2H), 8.85 (d, J = 5.1 Hz, 2H), 8.94 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.59, 52.05, 63.48, 64.71, 66.01, 68.84, 69.03, 71.45, 120.74, 125.27, 138.42, 138.80, 139.20, 140.87, 140.90, 141.79, 141.84, 142.14, 142.16, 142.90, 142.95, 142.97, 143.04, 143.82, 143.85, 144.52, 144.57, 144.58, 144.63, 144.65, 144.86, 145.06, 145.08, 145.11, 145.14, 145.15, 145.21, 145.23, 145.30, 150.16, 156.47, 163.36, 163.60, 165.06; IR (KBr): $\tilde{\nu}$ = 1739 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (186900), 325 (57490), 392 (sh, 8640), 402 (sh, 6230), 413 (sh, 4700), 426 (4470), 481 (2550), 686 nm (240); MS: see Table 1; $C_{150}H_{32}N_2O_{14} \cdot 2.6\,CH_2Cl_2$ (2306.8): calcd C 79.46, H 1.63, N 1.21; found C 79.25, H 1.90, N 1.54.

4′-[2-(2-Hydroxyethoxy)ethoxy]-2,2′:6′,2″-terpyridine (**17**): A mixture of **15** (1 g, 4.0 mmol), K_2CO_3 (1.7 g, 12.3 mmol) and NaI (0.6 g, 4.0 mmol) in anhydrous DMF was stirred at 70 °C for 30 min. 2-(2-Chloroethoxy)ethanol (527 mg, 4.23 mmol) was then added dropwise to the suspension and the reaction mixture was stirred at 70 °C for 20 h. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed sucessively with aq NaOH (2N), saturated aq $NaHCO_3$ and water, dried ($MgSO_4$), filtered and evaporated to dryness to yield **17** (1.12 g, 82%). Colourless microcrystalline solid; m.p. 113–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.17 (br t, J = 5.8 Hz, 1H), 3.65–3.67 (m, 2H), 3.74–3.76 (m, 2H), 3.88–3.90 (m, 2H), 4.38–4.40 (m, 2H), 7.27–7.31 (m, 2H), 7.81 (dt, J = 7.7, 1.8 Hz, 2H), 8.07 (s, 2H), 8.57 (d, J = 8.0 Hz, 2H), 8.65 (d, J = 4.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.69, 67.85, 69.82, 72.81, 107.72, 121.31, 123.75, 136.76, 148.94, 155.98, 156.96, 167.04; MS (MALDI-TOF): m/z = 339 [M^++H], 361 [M^++Na], 378 [M^++K]; $C_{19}H_{19}N_3O_3$ (337.4): calcd C 67.6, H 5.7, N 12.4; found C 67.4, H 5.5, N 12.4.

2-[2-(2,2′:6′,2″-Terpyridyl-4′-oxy)ethoxy]ethyl ethyl malonate (**13**): Compound **17** (1.05 g, 3.11 mmol) was treated with ethyl malonylchloride (0.515 g, 3.4 mmol) and pyridine (0.28 mL, 3.45 mmol) in CH_2Cl_2 (50 mL) according to the procedure described for (±)-**6**. After standard work-up, column chromatography (SiO_2, $CHCl_3$/2% satd methanolic NH_3) yielded **13** (1.0 g, 70%). Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.1 Hz, 3H), 3.41 (s, 2H), 3.81 (m, 2H), 3.90–3.92 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 4.31–4.33 (m, 2H), 4.37–4.39 (m, 2H), 7.28–7.33 (m, 2H), 7.83 (dt, J = 7.7, 1.8 Hz, 2H), 8.03 (s, 2H), 8.59 (d, J = 8.0 Hz, 2H), 8.66 (d, J = 4.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.00, 41.42, 61.48, 64.49, 67.69, 69.15, 69.37, 107.36, 121.27, 123.78, 136.72, 148.98, 155.97, 157.12, 166.40, 166.59, 166.85; MS (MALDI-TOF): m/z = 52 [M^++H], 474 [M^++Na], 491 [M^++K]; $C_{24}H_{25}N_3O_6 \cdot 1/3\,H_2O$ (457.5): calcd C 63.0, H 5.7, N 9.2; found C 63.1, H 5.6, N 9.3.

2-{2-[(2,2′:6′,2″-Terpyridin-4′-yl)oxy]ethoxy}ethyl ethyl 2-bromomalonate (**19**): Compound **13** (500 mg, 1.10 mmol) was treated with DBU (206 mg, 1.32 mmol) and CBr_4 (458 mg, 1.37 mmol) in THF (50 mL) according to the procedure described for (±)-**8**. After standard work-up, the resulting product (580 mg) was used in the next step without further purification. Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.1 Hz, 3H), 4.25 (q, J = 7.1 Hz, 2H), 4.46–4.48 (m, 4H), 4.64–4.66 (m, 4H), 4.92 (s, 1H), 7.30–7.35 (m, 2H), 7.83 (dt, J = 7.7, 1.8 Hz, 2H), 8.03 (s, 2H), 8.60 (d, J = 8.0 Hz, 2H), 8.66 (d, J = 4.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.81, 42.11, 63.25, 66.08, 67.71, 68.86, 69.42, 107.37, 121.29, 123.82, 136.76, 148.98, 155.90, 157.08, 164.30, 164.63, 166.83; MS (MALDI-TOF): m/z = 531 [M^++H], 452 [M^+ − Br+H].

2-[2-(Tosyloxy)ethoxy]ethyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (**21**): A solution of TsCl (1.22 g, 6.38 mmol) in CH_2Cl_2 (20 mL) was added dropwise in 20 min under N_2 to a stirred solution of **10** (300 mg, 0.319 mmol) in CH_2Cl_2/pyridine 8:2 (100 mL) at −2 °C. The solution was warmed slowly to RT (2 h) and stirred for 10 h at this temperature. The resulting CH_2Cl_2 solution was washed twice with saturated aq NH_4Cl, then water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/hexane 4:1) yielded 242 mg (0.221 mmol, 69%) of pure **21**. Dark red solid; m.p. > 280 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (t, J = 7.1 Hz, 3H), 2.45 (s, 3H), 3.73 (t, J = 5.0 Hz, 2H), 3.82 (t, J = 5.0 Hz, 2H), 4.17 (t, J = 5.0 Hz, 2H), 4.56 (q, J = 7.1 Hz, 2H), 4.58 (m, 2H), 7.36 (d, J = 7.9 Hz, 2H), 7.81 (d, J = 7.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.30, 21.74, 52.09, 63.60, 65.90, 68.80, 68.91, 69.07, 71.50, 127.96, 129.94, 132.95, 138.86, 139.21, 140.93, 140.94, 141.82, 141.90, 142.19, 142.20, 142.21, 142.96, 143.04, 143.10, 143.88, 143.89, 144.58, 144.63, 144.69, 144.91, 145.16, 145.29, 163.41, 163.60; IR (KBr): $\tilde{\nu}$ = 1744 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (103800), 326 (30160), 392 (sh, 3780), 402 (sh, 2560), 413 (sh, 1840), 426 (1910), 492 (1090), 688 nm (150); MS (FAB): m/z (%) = 1092 (47) [M^+], 720 (100) [C_{60}^+]; $C_{76}H_{20}O_8S \cdot 0.8\,CH_2Cl_2$ (1161.0): calcd C 79.4, H 1.9 ; found C 79.6, H 2.0.

2-{2-[(2,2′:6′,2″-Terpyridin-4′-yl)oxy]ethoxy}ethyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (**2**)

Method 1: Compound **19** (500 mg, 0.94 mmol) was treated with DBU (171 mg, 1.13 mmol) and C_{60} (814 mg, 1.13 mmol) in toluene (300 mL) according to the procedure described for (±)-**9**. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/3% satd methanolic NH_3) to afford **2** (570 mg, 52%). Dark brown powder; m.p. > 270 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (t, J = 7.1 Hz, 3H), 3.96–4.00 (m, 4H), 4.36–4.38 (m, 2H), 4.56 (q, J = 7.1 Hz, 2H), 4.69–4.71 (m, 2H), 7.30–7.33 (m, 2H), 7.83 (dt, J = 7.7, 1.8 Hz, 2H), 8.02 (s, 2H), 8.59 (d, J = 8.0 Hz, 2H), 8.66 (d, J = 4.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.21, 52.13, 63.50, 66.15, 67.91, 68.31, 69.13, 69.48, 71.50, 107.45, 121.34, 123.82, 136.72, 138.76, 139.24, 140.87, 141.81, 142.13, 142.14, 142.87, 142.90, 142.91, 142.96, 142.99, 143.80, 143.84, 144.53, 144.54, 144.55, 144.59, 144.60, 144.62, 144.82, 145.07, 145.09, 145.10, 145.14, 145.17, 145.19, 145.40, 145.86, 146.37, 149.01, 155.96, 157.17, 163.44, 163.68, 166.79; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 (130800), 325 (36150), 393 (sh, 5170), 401 (sh, 3950), 413 (sh, 2920), 426 (2800), 483 (1770), 689 nm (160); MS: see Table 1; $C_{84}H_{23}N_3O_6 \cdot 2\,H_2O$ (1206.2): calcd C 83.65, H 2.26, N 3.48; found C 83.35, H, 2.47, N, 3.93.

Method 2: A suspension of **15** (100 mg, 0.4 mmol) and K_2CO_3 (115 mg, 0.8 mmol) in DMF (10 mL) was stirred for 15 min at 60 °C. **21** (250 mg, 0.23 mmol) was added and the resulting mixture was stirred for 4 h at 60 °C. The suspension was then poured in water (100 mL). The resulting precipitate was collected by filtration, washed successively with aq NaOH (0.1M), water and EtOH, dissolved in CH_2Cl_2, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/3% satd methanolic NH_3) yielded **2** (43 mg, 16%).

4′-(2-Hydroxyethoxy)-2,2′:6′,2″-terpyridine (**18**): A mixture of **16** (1.5 g, 4.8 mmol) and anhydrous $FeCl_2$ (0.6 g, 4.8 mmol) in dry ethylene glycol (30 mL) was refluxed for 3 h. After cooling, the purple reaction mixture was precipitated by addition of aq NH_4PF_6. The precipitate was collected on a pad of Celite and washed with water before being redissolved in MeCN. The deep purple solution was reduced to 10 mL and aq NaOH (0.5M, 100 mL) was added. The alkaline solution was carefully treated with H_2O_2 until disappearance of the purple colour. The resulting mixture was filtered and partial removal of the solvent caused a colourless solid to precipitate. After collection by filtration, the product was recrystallised from EtOH to afford **18** (0.90 g, 64%). Colourless crystals; m.p. 150–151 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (br t, J = 5.8 Hz, 1H), 3.99–4.01 (m, 2H), 4.31–4.33 (m, 2H), 7.29–7.33 (m, 2H), 7.82 (dt, J = 7.7, 1.8 Hz, 2H), 8.01 (s, 2H), 8.57 (d, J = 8.0 Hz, 2H), 8.63 (d, J = 4.8 Hz, 2H); MS (EI): m/z = 293 [M^+], $C_{17}H_{15}N_3O_2 \cdot 1/3\,H_2O$ (299.3): calcd C 68.2, H 5.3, N 14.0; found C 68.0, H 5.0, 13.9.

2-[(2,2′:6′,2″-Terpyridin-4′-yl)oxy]ethyl ethyl malonate (**14**): Compound **18** (0.8 g, 2.72 mmol) was treated with ethyl malonylchloride (0.463 g, 3.07 mmol) and pyridine (0.22 mL, 2.72 mmol) in CH_2Cl_2 (50 mL) according to the procedure described for **6**. After standard work-up, recrystallisation from EtOH yielded **14** (0.84 g, 70%). Colourless oil; m.p. 68.5–69 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.1 Hz, 3H), 3.43 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 4.45–4.47 (m, 2H), 4.56–4.58 (m, 2H), 7.28–7.33 (m, 2H), 7.83 (dt, J = 7.7, 1.8 Hz, 2H), 8.03 (s, 2H), 8.59 (d, J = 8.0 Hz, 2H), 8.66 (d, J = 4.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.01, 41.39, 61.60,

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63.35, 65.72, 107.29, 121.28, 123.87, 136.75, 149.02, 155.89, 157.25, 166.24, 166.51, 166.57; MS (MALDI-TOF): $m/z = 408$ [M^++H], 430 [M^++Na], 447 [M^++K]; $C_{22}H_{21}N_3O_5$ (407.4): calcd C 64.9, H 5.2, N 10.3; found C 64.8 , H 4.9, N 10.3.

2-[(2,2′:6′,2″-Terpyridin-4′-yl)oxy]ethyl ethyl 2-bromomalonate (**20**): Compound **14** (475 mg, 1.21 mmol) was treated with DBU (234 mg, 1.51 mmol) and CBr_4 (501 mg, 1.51 mmol) in THF (50 mL) according to the procedure described for (±)-**8**. After standard work-up, the resulting product (600 mg) was used in the next step without further purification. Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$ (t, $J = 7.1$ Hz, 3H), 4.25 (q, $J = 7.1$ Hz, 2H), 4.46–4.48 (m, 2H), 4.64–4.66 (m, 2H), 4.92 (s, 1H), 7.31–7.36 (m, 2H), 7.83 (dt, $J = 7.7$, 1.8 Hz, 2H), 8.03 (s, 2H), 8.60 (d, $J = 8.0$ Hz, 2H), 8.66 (d, $J = 4.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.81$, 42.02, 63.37, 64.83, 65.48, 107.26, 121.30, 123.92, 136.81, 149.00, 155.77, 157.22, 164.30, 165.22, 166.47; MS (MALDI-TOF): $m/z = 446$ [M^+ − Br+K], 509 [M^++Na], 526 [M^++K].

2-[(2,2′:6′,2″-Terpyridin-4′-yl)oxy]ethyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate (**3**): Compound **20** (530 mg. 1.0 mmol) was treated with DBU (182 mg, 1.2 mmol) and C_{60} (860 mg, 1.2 mmol) in toluene (300 mL) according to the procedure described for (±)-**9**. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/3% satd methanolic NH_3) to afford **3** (686 mg, 55%). Dark brown powder; m.p. > 270 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.45$ (t, $J = 7.1$ Hz, 3H), 4.53 (q, $J = 7.1$ Hz, 2H), 4.61–4.63 (m, 2H), 4.92–4.94 (m, 2H), 7.29–34 (m, 2H), 7.80 (dt, $J = 7.7$, 1.8 Hz, 2H), 8.02 (s, 2H), 8.57 (d, $J = 8.0$ Hz, 2H), 8.66 (d, $J = 4.8$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 14.22, 52.01, 63.59, 64.96, 65.66, 65.82, 71.43, 107.40, 121.32, 123.91, 136.77, 138.41, 139.51, 140.81, 140.95, 141.78, 141.86, 142.14, 142.15, 142.76, 142.87, 142.90, 142.91, 142.93, 142.98, 143.73, 143.85, 144.53, 144.58, 144.60, 144.63, 144.65, 144.82, 144.90, 144.94, 145.10, 145.13, 145.20, 145.22, 145.38, 149.02, 155.80, 157.32, 163.36, 163.66, 166.41; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 (119950) , 325 (32660), 393 (sh, 4270), 401 (sh, 3190), 413 (sh, 2250), 426 (2230), 486 (1360), 689 nm (130); MS: see Table 1; $C_{82}H_{19}N_3O_5 \cdot 5.5\,H_2O$ (1225.2): calcd C 80.39, H 2.47, N 3.43; found C 80.27, H 2.12, N 3.93.

Dimethyl 3-methylpentanedioate (**24**): A mixture of *p*-TsOH (0.25 g), **23** (25 g), MeOH (8.5 mL, 0.21 mol) and 2,2-dimethoxypropane (35.4 g, 0.34 mol) was stirred for 14 h at 45 °C. The solvents were removed in vacuo and the liquid residue distilled under high vacuum to yield **24** (24.1 g, 81%). Colourless oil; b.p. 106 °C/10 Torr (ref. [27] b.p. 110 °C/19 Torr).

1,5-Bis(2-pyridyl)-3-methylpentane-1,5-dione (**25**): *n*BuLi in hexanes (1.6 M, 85.6 mL, 0.137 mol) was added to a solution of TMEDA (20.5 mL, 0.137 mol) in dry THF (300 mL) at −78 °C under N_2. 2-Bromopyridine (13 mL, 0.137 mol) was then added dropwise and the temperature was raised to −55 °C; the resulting mixture was stirred for 30 min at this temperature then cooled to −78 °C and **24** (10 g, 0.057 mol) was added in one portion. The resulting mixture was stirred at −78 °C for 1 h and H_2O (100 mL) was added. The aq layer was acidified with 10% aq HCl (50 mL) and extracted with CH_2Cl_2 (200 mL). Neutralisation of the aq layer with 10% aq NaOH (60 mL) caused the product to separate as an oil. The latter was recovered by extraction with CH_2Cl_2. The organic extract was dried (Na_2SO_4), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/EtOAc 9:1) followed by recrystallisation from cold heptane yielded **25** (6.26 g, 41%). Colourless solid; m.p. 50–51 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.05$ (d, $J = 6.5$ Hz, 3H), 2.80–2.93 (m, 1H), 3.14–3.31 (m, 4H), 7.35–7.41 (m, 2H), 7.76 (dt, $J = 7.5$, 2.0 Hz, 2H), 7.97 (d, $J =$ 7.7 Hz, 2H), 8.58 (d, $J = 4.8$ H, 2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 20.50, 25.54, 44.36, 121.68, 126.90, 136.76, 148.78, 153.60, 201.00; IR (KBr): $\tilde{\nu} = 1700$ cm^{-1} (C=O); MS (FAB): $m/z = 269$ [M^++H]; $C_{16}H_{16}O_2N_2$ (268.3): calcd C 71.62, H 6.01, N 10.44; found C 71.53, H 6.07, N 10.40.

4′-Methyl-2,2′:6′,2″-terpyridine (**22**): A solution of **25** (2.4 g, 9.0 mmol) and ammonium acetate (6.0 g, 78 mmol) in glacial acetic acid (120 mL) was refluxed in air for 2 h. The resulting mixture was concentrated to 20 mL and poured into 10% aq NaOH (200 mL). The yellow precipitate was collected by filtration, washed with water and dried under high vacuum. Recrystallisation from cold heptane yielded pure **26** (1.7 g, 76%). Slightly yellow solid; m.p. 96–97 °C (ref. [23] m.p. 97–100 °C).

Ethyl (2,2′:6′,2″-terpyridin-4′-yl)acetate (**26**): MeLi in Et_2O (1.6 M, 1.4 mL, 2.24 mol) was added to a solution of 2,2,6,6-tetramethylpiperidine (0.42 mL, 2.5 mmol) in dry THF (5 mL) at −10 °C. After the resulting yellow solution was stirred for 15 min at −10 °C, a solution of **22** (0.5 g, 2 mmol) in THF (5 mL) was added. The resulting deep red solution was transferred over 1 h through a cannula to a cooled solution (−10 °C) of ethyl chloroformate (0.23 mL, 2.4 mmol) in THF (10 mL). The reaction mixture was then allowed to warm to RT, and stirred for a further 30 min before being quenched with water (50 mL). The THF was removed under reduced pressure, and the resulting emulsion was extracted with CH_2Cl_2 (150 mL); the organic extract was washed with brine (50 mL), dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, Hexane/Et_2NH 9:1) followed by recrystallisation from *n*-hexane yielded **26** (0.41 g, 64%). Colourless needles; m.p. 86–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.23$ (t, $J = 7.1$ Hz, 3H), 3.78 (s, 2H), 4.16 (q, $J =$ 7.1 Hz, 2H), 7.23–7.32 (m, 2H), 7.82 (dt, $J = 7.7$, 1.8 Hz, 2H), 8.37 (s, 2H), 8.58 (d, $J = 8.0$ Hz, 2H), 8.66 (d, $J = 4.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.11$, 40.95, 61.14, 121.24, 121.84, 123.74, 136.76, 144.89, 149.02, 155.61, 155.96, 170.15; IR (KBr): $\tilde{\nu} = 1736$ cm^{-1} (C=O); MS (FAB): $m/z = 320$ [M^++H], 247 [M^+ − COOEt+H]; $C_{19}H_{17}O_2N_3$ (319.4): calcd C 71.46, H 5.37, N 13.16; found C 71.47, H 5.36, N 13.25.

Ethyl bromo(2,2′:6′,2″-Terpyridin-4′-yl)acetate (**27**): Compound **26** (380 mg, 1.19 mmol) was treated with DBU (180 μL, 1.20 mmol) and CBr_4 (395 mg, 1.19 mmol) in THF (60 mL) according to the procedure described for (±)-**8**. After standard work-up, the resulting product (470 mg) was used in the next step without further purification. Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.1$ Hz, 3H), 4.10–4.31 (m, 2H), 5.44 (s, 1H), 7.24–7.34 (m, 2H), 7.80 (dt, $J = 7.7$, 1.8 Hz, 2H), 8.55 (d, $J = 8.0$ Hz, 2H), 8.59 (s, 2H), 8.66 (d, $J = 4.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.86$, 45.06, 62.83, 120.49, 121.22, 123.98, 136.82, 146.38, 149.11, 155.34, 156.08, 167.38; MS (FAB): $m/z = 400$ [M^++H], 354 [M^+ − EtO+2H], 247 [M^+ − COOEt − Br+2H].

Ethyl 61-(2,2′:6′,2″-terpyridin-4′-yl-)-1,2-methano-[60]-fullerene-61-carboxylate (**1**)

Method 1: Compound **27** (350 mg, 0.87 mmol) was treated with DBU (150 μL, 1.00 mmol) and C_{60} (751 mg, 1.04 mmol) in toluene (300 mL) according to the procedure described for (±)-**9**. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/3% satd methanolic NH_3) to afford **1** (705 mg, 78%). Dark brown powder; m.p. > 270 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.37$ (t, $J = 7.1$ Hz, 3H), 4.46 (q, $J = 7.1$ Hz, 2H), 7.37–7.40 (m, 2H), 7.91 (dt, $J = 7.7$, 1.8 Hz, 2H), 8.74 (d, $J = 8.0$ Hz, 2H), 8.77 (d, $J = 4.8$ Hz, 2H), 9.20 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.30$, 54.70, 63.29, 74.89, 121.42, 124.09, 136.87, 138.13, 138.51, 140.94, 140.97, 141.94, 142.16, 142.19, 142.20, 142.85, 142.94, 142.97, 143.07, 143.09, 143.42, 143.65, 143.92, 144.42, 144.43, 144.51, 144.63, 144.70, 144.72, 144.78, 145.13, 145.14, 145.18, 145.22, 145.39, 145.54, 145.92, 145.94, 146.80, 146.83, 149.32, 155.59, 155.91, 165.60; IR (KBr): $\tilde{\nu} =$ 1740 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 (119700), 320 (43800), 394 (sh, 4900), 403 (sh, 3550), 415 (sh, 2540), 428 (3400), 483 (1700), 688 nm (140); MS: see Table 1; $C_{79}H_{15}O_2N_3 \cdot 1.5\,H_2O$ (1065.0): calcd C 89.10, H 1.69, N 3.95; found C 89.13, H 1.82, N 4.26.

Method 2: Compound **26** (100 mg, 0.311 mmol) was treated with DBU (100 μL, 0.68 mmol), I_2 (80 mg, 0.31 mmol) and C_{60} (223 mg. 0.31 mmol) in toluene (300 mL) according to the procedure described for (±)-**9**. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/3% satd methanolic NH_3) to afford **1** (85 mg, 26%).

[Ru(4)(bipy)$_2$][PF$_6$]$_2$: A mixture of *cis*-$(bipy)_2Cl_2$ (35 mg, 0.072 mmol) and $AgBF_4$ (20 mg, 1.00 mmol) in acetone (10 mL) was refluxed for 2 h. After cooling and filtration, the solvent was evaporated and the residue taken up in DMF (20 mL); **4** (150 mg, 0.072 mmol) was then added. The resulting mixture was refluxed for 3 h. After cooling, the crude product was precipitated as its PF_6 salt by addition of a methanolic solution of NH_4PF_6 followed by water. The brown solid was filtered, washed with water, MeOH and Et_2O. Column chromatography (SiO_2, CH_2Cl_2/15% MeOH) yielded [Ru(**4**)$(bipy)_2$][PF_6]$_2$ (72 mg, 36%). Dark brown solid; m.p. > 280 °C; ^{1}H NMR (CD_2Cl_2, 200 MHz): $\delta = 1.33$ (t, $J = 7.1$ Hz, 6H), 3.90 (m, 8H), 4.50 (q, $J = 7.1$ Hz, 4H), 4.55 (m, 4H), 4.65 (m, 4H), 7.44–7.55 (m, 4H), 7.65–7.71 (m, 4H), 7.95–8.15 (m, 8H), 8.43–8.47 (m, 4H), 9.07(s, 2H); IR (KBr): $\tilde{\nu} = 1731$ cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 (236600), 285 (sh, 143100), 310 (98200), 364 (sh, 40500), 393 (sh, 23100), 402 (sh, 20800), 413 (sh, 19300), 426 (19900), 480 (17700), 681 (1260); MS: see Table 1; $C_{170}H_{48}O_{14}N_6P_2F_{12}Ru \cdot 2\,H_2O$ (2825.3): calcd C 72.27, H 1.86, N 2.97; found C 72.46, H 1.82, N 3.28.

[Ru(2)(tpy)][PF$_6$]$_2$: A mixture of [Ru(tpy)Cl$_3$] (29 mg, 0.065 mmol) and AgBF$_4$ (35 mg, 0.18 mmol) in acetone (10 mL) was refluxed for 2 h. After cooling and filtration, DMF (20 mL) was added to the filtrate and acetone removed in vacuo. The resulting blue solution was added to a solution of **2** (70 mg, 0.06 mmol) in DMF (5 mL) and the mixture was refluxed for 3 h. After cooling, the crude product was precipitated as its PF_6 salt by addition of aq NH_4PF_6 (0.02 M, 50 mL). The brown solid was filtered, washed with water, MeOH and Et_2O. Column chromatography (SiO_2, CH_2Cl_2/MeOH 8:2) yielded [Ru(**2**)(tpy)][PF$_6$]$_2$ (56 mg, 52%). Dark red powder; m.p. > 270 °C; ^{1}H—NMR (300 MHz, CD_3CN): $\delta = 1.45$ (t, $J = 7.1$ Hz, 3H), 4.01–4.03 (m, 2H), 4.07–4.09 (m, 2H), 4.54 (q, $J = 8.1$ Hz, 2H), 4.60–4.62 (m, 2H), 4.74–4.76 (m, 2H), 7.06–7.11 (m, 2H), 7.12–7.16 (m, 2H), 7.24 (d, $J = 5.4$ Hz, 2H), 7.33 (d, $J = 5.4$ Hz, 2H), 7.84 (dt, $J = 7.7$, 1.8 Hz, 2H), 7.89 (dt, $J = 7.7$, 1.8 Hz, 2H), 8.28 (s, 2H), 8.34 (t, $J = 8.1$ Hz, 1H), 8.42 (d, $J = 8.1$ Hz, 2H), 8.45 (d, $J = 8.1$ Hz, 2H), 8.69 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 14.48$, 53.87, 64.77, 67.14, 69.72, 70.93, 72.68, 112.19, 124.51, 125.20, 125.42, 128.36, 128.40, 136.13, 138.77, 138.81, 139.73, 139.88, 141.74, 141.80, 142.74, 142.91, 143.00, 143.72, 143.79, 143.83, 143.93, 144.60, 144.64, 145.37, 145.52, 145.56, 145.64, 145.99, 146.19, 146.41, 146.48, 152.97, 153.58, 156.70, 156.83, 158.78, 159.11, 164.02, 164.19, 167.06; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (140350), 310 (91350), 327 (sh, 60120) 394 (sh, 8720), 403 (sh, 8000), 415 (sh, 8410), 426 (10400), 482 (20010), 686 nm (270); MS: see Table 1.

[Ru(3)(tpy)][PF$_6$]$_2$: This complex was prepared from [Ru(tpy)Cl$_3$] (29 mg, 0.065 mmol), AgBF$_4$ (35 mg, 0.18 mmol) and **3** (68 mg, 0.06 mmol) according to the procedure described for [Ru(**2**)(tpy)][PF$_6$]$_2$. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 8:2) to afford [Ru(**3**)(tpy)][PF$_6$]$_2$ (50 mg, 48%). Dark red powder; m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN): $\delta =$ 1.44 (t, $J = 7.1$ Hz, 3H), 4.55 (q, $J = 7.1$ Hz, 2H), 4.91–4.93 (m, 2H), 5.08–5.10 (m, 2H), 7.06–7.11 (m, 2H), 7.10–7.14 (m, 2H), 7.25–7.29 (m, 2H), 7.81 (dt, $J = 7.7$, 1.8 Hz, 2H), 7.87 (dt, $J = 7.7$, 1.8 Hz, 4H), 8.28 (s, 2H), 8.35 (t, $J = 8.1$ Hz, 1H), 8.40 (d, $J = 8.1$ Hz, 2H), 8.45 (d, $J = 8.1$ Hz, 2H), 8.70 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 14.37$, 53.85, 65.04, 66.12, 66.34, 68.77, 72.77, 112.15, 124.67, 125.37, 125.60, 128.54, 138.90, 139.61, 140.22, 141.84, 141.97, 142.88, 143.03, 143.22, 143.82, 144.03, 144.63, 144.84, 145.49, 145.69, 146.16, 146.26, 146.79, 152.90, 153.71, 156.74, 157.02, 158.73, 159.23, 163.98, 164.22, 166.47; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (140580), 308 (91030), 327 (sh, 67170) 394 (sh, 8840), 403 (sh, 7950), 414 (sh, 8130), 426 (10160), 482 (18560), 686 nm (260); MS: see Table 1.

[Ru(1)(tpy)][PF$_6$]$_2$: This complex was prepared from [Ru(tpy)Cl$_3$] (110 mg, 0.25 mmol), AgBF$_4$ (150 mg, 0.76 mmol) and **1** (250 mg, 0.25 mmol) according to the procedure described for [Ru(**2**)(tpy)][PF$_6$]$_2$. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 85:15) to afford [Ru(**1**)(tpy)][PF$_6$]$_2$ (303 mg, 73%). Dark red powder; m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN): $\delta = 1.49$ (t, $J = 7.1$ Hz, 3H), 4.62 (q, $J = 7.1$ Hz, 2H), 7.16–7.22 (m, 4H), 7.33 (d, $J = 5.4$ Hz, 2H), 7.39 (d, $J = 5.4$ Hz, 2H), 7.93 (dt, $J = 7.7$, 1.8 Hz, 2H), 7.95 (dt, $J = 7.7$, 1.8 Hz, 2H), 8.44 (t, $J = 8.1$ Hz, 1H), 8.51 (d, $J = 8.1$ Hz, 2H), 8.66 (d, $J = 8.1$ Hz, 2H), 8.77 (d, $J = 8.0$ Hz, 2H), 9.58 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.66$, 53.60, 54.25, 63.88, 74.85, 123.82, 124.51, 124.92, 127.12, 127.53, 127.69, 135.65, 136.55, 137.92 (2C), 138.16, 138.22, 139.09, 139.24, 140.81, 141.07, 141.89, 142.08, 142.16, 142.22, 142.87, 143.08 (2C), 143.12, 143.23, 143.74, 143.97, 144.29, 144.55, 144.59, 144.67, 144.77, 144.82, 145.22, 145.25, 145.33, 145.44, 145.83, 146.00 (2C), 146.52, 152.42 (2C), 155.70, 156.41, 157.93, 158.50, 165.41; IR (KBr): $\tilde{\nu} =$ 1727 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (128900), 310 (91500), 325 (sh, 73960), 394 (sh, 9110), 415 (sh, 7990), 428 (9680), 481 (19950), 684 nm (280); MS: see Table 1; $C_{94}H_{26}N_6O_2P_2F_{12}Ru \cdot 3H_2O$ (1716.3): calcd C 65.78, H 1.88, N 4.90; found C 65.48, H 1.85, N 5.11.

[Ru(26)(tpy)][PF$_6$]$_2$. This complex was prepared from [Ru(tpy)Cl$_3$] (176 mg, 0.17 mmol), AgBF$_4$ (112 mg, 0.55 mmol) and **26** (55 mg, 0.17 mmol) according to the procedure described for [Ru(**2**)(tpy)][PF$_6$]$_2$. Standard work-up afforded [Ru(**26**)(tpy)][PF$_6$]$_2$ (122 mg, 76%). Dark red microcrystalline solid; m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN): $\delta =$ 1.28 (t, $J = 7.1$ Hz, 3H), 4.21 (s, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 7.08–7.20 (m, 4H), 7.32 (d, $J = 5.4$ Hz, 4H), 7.90 (dt, $J = 7.7$, 1.8 Hz, 4H), 8.41 (t, $J =$ 8.1 Hz, 1H), 8.43 (s, 2H), 8.48 (d, $J = 8.1$ Hz, 2H), 8.70 (s, 2H), 8.72 (d, $J =$ 8.1 Hz, 2H); IR (KBr): $\tilde{\nu} = 1729$ cm^{-1} (C=O); MS: see Table 1; $C_{34}H_{28}N_6O_2P_2F_{12}Ru \cdot 2.5H_2O$ (988.7): calcd C 41.31, H 3.36, N 8.50; found C 41.24, H 3.14, N 8.32.

[Ru(2)(4′-Me$_2$Ntpy)][PF$_6$]$_2$: This complex was prepared from [Ru(4′-Me$_2$Ntpy)Cl$_3$] (31 mg, 0.065 mmol), AgBF$_4$ (35 mg, 0.18 mmol) and **2** (70 mg, 0.060 mmol) according to the procedure described for [Ru(**2**)(tpy)][PF$_6$]$_2$. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 85:15) to afford [Ru(**2**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ (21 mg, 23%). Dark red powder; m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN): $\delta = 1.46$ (t, $J = 7.1$ Hz, 3H), 3.44 (s, 6H), 4.02–4.04 (m, 2H), 4.07–4.09 (m, 2H), 4.55 (q, $J = 7.1$ Hz, 2H), 4.58–4.60 (m, 2H), 4.75–4.77 (m, 2H), 7.03–7.08 (m, 2H), 7.12–7.17 (m, 2H), 7.23 (d, $J = 5.4$ Hz, 2H), 7.41 (d, $J = 5.4$ Hz, 2H), 7.83 (dt, $J = 7.7$, 1.8 Hz, 2H), 7.85 (dt, $J = 7.7$, 1.8 Hz, 2H), 7.90 (s, 2H), 8.27 (s, 2H), 8.41 (d, $J =$ 8.1 Hz, 2H), 8.44 (d, $J = 8.1$ Hz, 2H); ^{13}CNMR (125 MHz, CD_3CN): $\delta =$ 14.59, 40.87, 53.83, 64.87, 67.24, 69.83, 70.89, 72.78, 107.49, 111.96, 124.73, 125.28, 127.88, 128.44, 138.37, 138.47, 139.84, 139.97, 141.83, 141.89, 142.83, 143.01, 143.10, 143.83, 143.89, 143.92, 144.70 144.74, 145.45, 145.62, 146.09, 146.19, 146.52, 146.59, 153.25, 153.29, 155.27, 156.08, 157.82, 159.36, 160.20, 164.11, 164.29, 166.16; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 259 (151280), 303 (89700), 326 (sh, 57240), 392 (sh, 9570), 415 (sh, 8090), 428 (9840), 497 (21860), 687 nm (220); MS: see Table 1.

[Ru(3)(4′-Me$_2$Ntpy)][PF$_6$]$_2$: This complex was prepared from [Ru(4′-Me$_2$Ntpy)Cl$_3$] (46 mg, 0.095 mmol), AgBF$_4$ (53 mg, 0.27 mmol) and **3** (100 mg, 0.09 mmol) according to the procedure described for [Ru(**2**)(tpy)][PF$_6$]$_2$. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 85:15) to afford [Ru(**3**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ (35 mg, 22%). Dark red powder; m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN): $\delta = 1.48$ (t, $J = 7.1$ Hz, 3H), 3.44 (s, 6H), 4.57 (q, $J = 7.1$ Hz, 2H), 4.89–4.91 (m, 2H), 5.09–5.11 (m, 2H), 7.00–7.05 (m, 2H), 7.11–7.18 (m, 4H), 7.41 (d, $J = 5.4$ Hz, 2H), 7.79–7.87 (m, 4H), 7.89 (s, 2H), 8.26 (s, 2H), 8.38 (d, $J = 8.1$ Hz, 2H), 8.43 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 14.48$, 40.76, 53.83, 64.89, 66.02, 66.17, 68.52, 72.66, 107.40, 111.86, 124.66, 125.27, 127.84, 128.38, 138.20, 138.40, 139.35, 140.07, 141.30, 141.73, 141.87, 142.73, 142.76, 142.83, 143.06, 143.65, 143.84, 143.89, 144.44, 144.69, 145.24, 145.32, 145.41, 145.56, 145.64, 145.86, 145.97, 146.02, 146.14, 146.76, 153.00, 153.18, 155.10, 155.99, 157.79, 159.11, 160.10, 163.88, 164.15, 165.33; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 259 (154380), 304 (89600), 324 (sh, 66840) 393 (sh, 9870), 403 (sh, 7890), 414 (sh, 7350), 427 (8620), 499 (18890), 687 (210); MS: see Table 1.

[Ru(1)(4′-Me$_2$Ntpy)][PF$_6$]$_2$: This complex was prepared from [Ru(4′-Me$_2$Ntpy)Cl$_3$] (72 mg, 0.15 mmol), AgBF$_4$ (86 mg, 0.43 mmol) and **1** (150 mg, 0.15 mmol) according to the procedure described for [Ru(**2**)(tpy)][PF$_6$]$_2$. After standard work-up, the brown crude material was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 85:15) to afford [Ru(**1**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ (65 mg, 25%). Dark red powder; m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN): $\delta = 1.48$ (t, $J = 7.1$ Hz, 3H), 3.48 (s, 6H), 4.62 (q, $J = 7.1$ Hz, 2H), 7.07–7.10 (m, 2H), 7.21 (d, $J = 5.4$ Hz, 2H), 7.25–7.28 (m, 2H), 7.54 (d, $J = 5.4$ Hz, 2H), 7.87 (dt, $J = 7.7$, 1.8 Hz, 2H), 7.95 (dt, $J = 7.7$, 1.8 Hz, 2H), 7.96 (s, 2H), 8.50 (d, $J = 8.1$ Hz, 2H), 8.65 (d, $J =$ 8.1 Hz, 2H), 9.54 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.67$, 39.87, 53.79, 63.82, 74.94, 106.59, 123.89, 124.59, 126.87, 126.92, 127.68, 137.67, 137.87 (2C), 139.10 (2C), 140.80 (2C), 141.05, 141.87, 142.09, 142.14, 142.21, 142.85, 143.06 (2C), 143.10 (2C), 143.17, 143.72, 143.96, 144.30, 144.53, 144.58, 144.66, 144.75, 144.8 (2C), 145.21, 145.24, 145.31, 145.46, 145.83, 146.09 (2C), 146.61, 151.97, 152.51, 153.61, 156.67, 158.23, 158.95, 165.09; IR (KBr): $\tilde{\nu} = 1726$ cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 (149300), 310 (90500), 324 (sh, 78980), 394 (sh, 9610), 415 (sh 7840), 428 (8800), 470 (16180), 504 (22600); MS: see Table 1; $C_{96}H_{31}N_7O_2P_2F_{12}Ru \cdot 12H_2O$ (1921.5): calcd C 60.01, H 2.89, N 5.10; found C 60.17, H 3.02, N 5.19.

[Ru(26)(4′-Me$_2$Ntpy)][PF$_6$]$_2$: This complex was prepared from [Ru(4′-Me$_2$Ntpy)Cl$_3$] (75 mg, 0.15 mmol), AgBF$_4$ (94 mg, 0.50 mmol) and **26** (94 mg, 0.15 mmol) according to the procedure described for [Ru(**2**)(tpy)][PF$_6$]$_2$. After standard work-up, the red crude material was subjected to column chromatography (SiO_2, CH_3CN/ satd aq KNO_3/H_2O 14:2:1) to afford [Ru(**26**)(4′-Me$_2$Ntpy)][PF$_6$]$_2$ (55 mg, 37%). Dark red powder; m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN): $\delta = 1.38$ (t, $J = 7.1$ Hz, 3H), 3.46 (s, 6H), 4.19 (s, 2H), 4.32 (q, $J = 7.1$ Hz, 2H), 7.04–7.06 (m, 2H), 7.18–7.21 (m, 2H), 7.21 (d, $J = 5.4$ Hz, 2H), 7.46 (d, $J = 5.4$ Hz, 2H), 7.87 (dt, $J =$ 7.7, 1.8 Hz, 4H), 7.93 (s, 2H), 8.43 (d, $J = 8.1$ Hz, 2H), 8.47 (d, $J = 8.1$ Hz, 2H), 8.66 (s, 2H); IR (KBr): $\tilde{\nu} = 1729$ cm^{-1} (C=O); MS: see Table 1.

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