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Electronic Communication in Luminescent Dicyanorhenate-Bridged Homotrinuclear Rhenium(I) Complexes

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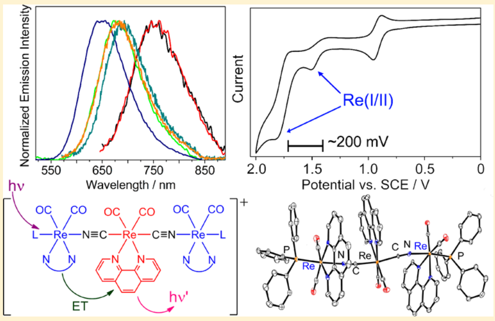
S *Supporting Information*

ABSTRACT: A series of cyano-bridged homotrinuclear Re(I) complexes with the general formula of $\{[Re]'[Re][Re]'\}^+$ $\{[Re]' = -[Re^I(CO)_2(LL)(X)]$; $[Re] = -[(NC)Re^I(CO)_2(phen)(CN)]-$; LL = diimine, diphosphine, or two carbonyl ligands; X = triphenylphosphine or carbonyl ligand$\}$ and the corresponding mononuclear complex analogues were synthesized. The structures of most of the trinuclear Re(I) complexes have been determined by X-ray crystallography. The relative orientations of peripheral to central Re(I) units in these structures vary considerably. The photophysical properties of these trinuclear Re(I) complexes have been examined. Except for the trinuclear Re(I) complex with Br_2phen ligand, all the other triads display orange to red photoluminescence derived from the ^{3}MLCT [dπ(Re) → π*(phen)] origin of the central Re(I) unit, suggestive of efficient energy transfer between the peripheral chromophores and the central unit. In addition to the efficient energy transfer processes between the Re(I) chromophores in these trinuclear complexes, the ability of the [NC−Re−CN] bridging ligands for electronic coupling between the rhenium metal centers is evidenced by ca. 0.2−0.3 V separation of the two rhenium metal-based oxidation potentials of the chemically equivalent peripheral units.



■ INTRODUCTION

Cyano-bridged polynuclear transition metal complexes have attracted intensive research efforts in the past few decades. On the basis of the rich coordination chemistry of the cyanide ligand ($^-$:C≡N:) and its ambidentate nature, which enable construction of polynuclear complexes of different polynuclearity,[1] geometries,[2] and/or dimensionality,[3] a large number of cyano-bridged polynuclear transition metal complexes have been exploited for diverse applications such as molecular devices,[4] molecular sieves,[3d,e,5] nanoparticles,[6] and ion sensors.[7] In contrast, cyano-bridged polynuclear species are also ideal candidates for the study of photoinduced intramolecular electron and energy-transfer processes.[8] Through spectroscopic, electrochemical,[9] and time-resolved spectroscopic studies[10] of these complexes, we gain a fundamental understanding useful for the design of functional polynuclear complexes with applications in many different areas such as photocatalysis,[11] electrocatalysis,[12] and antenna systems.[13]

Cyano Ru(II) polypyridine complexes represent the most popular building blocks for the construction of photoactive cyano-bridged polynuclear complexes.[8e,9b,14] Selected examples include the use of trinuclear Ru(II) complexes *cis*-$[(CN)(bpy)_2Ru{-}CN{-}Ru(LL)_2{-}NC{-}Ru(bpy)_2(CN)]^n$ (bpy = 2,2′-bipyridine, LL = 4,4′-dicarboxy-2,2′-bipyridine) as photosensitizers in TiO_2-based photovoltaic cells.[13a,b] In contrast, photoactive cyano-bridged complexes comprising Re(I) luminophores are less common,[15] although there are reports of the heterotrinuclear Re(I)−Ru(II) system, $[(CO)_3(bpy)Re(\mu\text{-}NC)Ru(bpy)_2(\mu\text{-}CN)Re(bpy)(CO)_3]^{2+}$,[15a] with an efficient intramolecular energy transfer process and the cyano-bridged pentanuclear Re(I)−Ru(II) complex, $[(phen)(CO)_3Re(CN)[Ru(bpy)_2(CN)]_3Ru(bpy)_2(CN)]^{4+}$, capable of functioning as antenna-sensitizer system.[16] While cyano-bridged homotrinuclear Ru(II) complexes with effective metal−metal electronic coupling have been recently reported by Pieslinger et al.,[17] the corresponding study of cyano-bridged homonuclear Re(I) complexes has only been confined to the dinuclear one[15a] owing to the lack of synthetic methodology for dicyano Re(I) diimine complexes.

On the basis of our recent work on dicarbonyl dicyanorhenate diimine complexes, *cis,trans*-$[Re(CO)_2(CN)_2(N{-}N)]$,[18] we herein describe the syntheses and study of a new series of cyano-bridged triads with general formula of $\{[Re]'[Re][Re]'\}^+$ $\{[Re]' = -[Re^I(CO)_2(LL)(X)]$; $[Re] = -[(NC)Re^I(phen)(CO)_2(CN)]-$; LL = diimine, diphosphine or two carbonyl ligands; X = triphenylphosphine or carbonyl ligand$\}$. Through photophysical and electrochemical properties, the electronic coupling and communication in these trinuclear complexes have been investigated.

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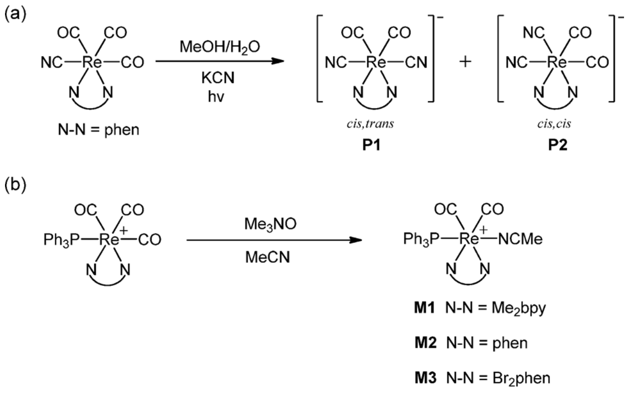
RESULTS AND DISCUSSION

Synthesis and Characterization. *cis,trans*-[Re(CO)$_2$(CN)$_2$(phen)](^{n}Bu$_4$N) (**P1**) was prepared by photoligand substitution reaction of [Re(CO)$_3$(phen)(CN)][19] with a 1000-fold excess of cyanide according to the synthetic procedures previously reported by us.[18] When a smaller amount of cyanide (100-fold excess) was used in the photoreaction, a mixture of **P1** and *cis,cis*-isomer (**P2**) was formed (Scheme 1a). These isomers can be separated by column chromatography on silica gel. To synthesize the trinuclear Re(I) complexes bridged by these metalloligands, [Re(CO)$_2$(CN)$_2$(N−N)]$^-$ (**P1** and **P2**), precursor complexes with labile acetonitrile (MeCN) or triflate (OTf$^-$) ligand, *cis,trans*-[Re(CO)$_2$(PPh$_3$)(N−N)(MeCN)](OTf)[20] [N−N = Me$_2$bpy (**M1**), phen (**M2**), and Br$_2$phen (**M3**)] (Scheme 1b), *fac*-[Re(CO)$_3$(dppe)(OTf)][21] [dppe = 1,2-bis(diphenylphosphino)ethane] and [Re(CO)$_5$(OTf)][22] were prepared according to reported procedures for structurally related complexes. The reactions of 2.3 mol equiv of these complexes with **P1** or **P2** gave the target trinuclear Re(I) complexes (Scheme 2): *trans*-[(PPh$_3$)(N−N)(CO)$_2$Re^I(μ-NC)Re^I(CO)$_2$(phen)(μ-CN)Re^I(CO)$_2$(N−N)(PPh$_3$)]$^+$ (N−N = Me$_2$bpy: **1**; N−N = phen: **2**; N−N = Br$_2$phen: **3**), *trans*-[(dppe)(CO)$_3$Re^I(μ-NC)Re^I(CO)$_2$(phen)(μ-CN)Re^I(CO)$_3$(dppe)]$^+$ (**4**), *trans*-[(CO)$_5$Re^I(μ-NC)Re^I(CO)$_2$(phen)(μ-CN)Re^I(CO)$_5$]$^+$ (**5**), and *trans*- and *cis*-[(phen)(CO)$_3$Re^I(μ-NC)Re^I(CO)$_2$(phen)(μ-CN)Re^I(CO)$_3$(phen)]$^+$ (**6** and **7**, respectively). These ligand substitution reactions were carried out at 50 °C for acetonitrile complexes and 30 °C for triflate complexes. Purification of these trinuclear complexes can be achieved by column chromatography, and the excess tetra-*n*-butyl ammonium salts from these reactions can be removed by washing the dichloromethane solution of the complexes with copious amounts of water.

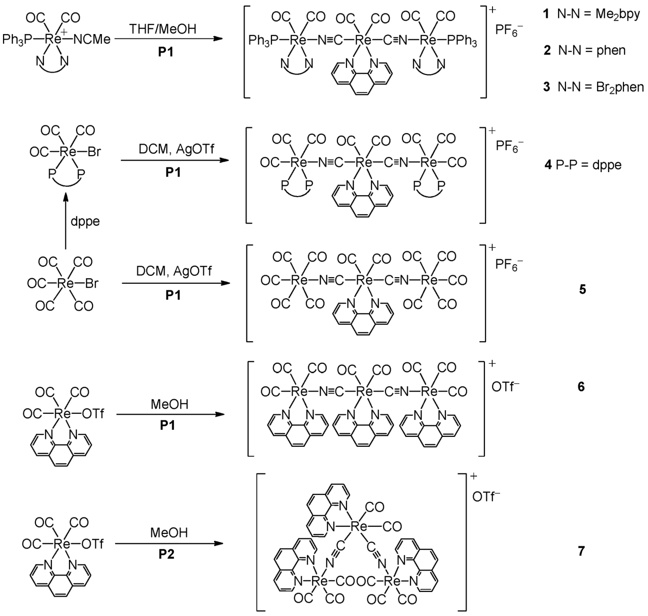
Scheme 1. Synthetic Routes for Synthetic Precursors for Trinuclear Re(I) Complexes



The identities of all of the complexes were confirmed by the ^{1}H NMR spectroscopy, IR spectroscopy, ESI mass spectrometry, and elemental analyses. The structures of trinuclear complexes **2**−**6** have also been determined by X-ray crystallography.

NMR and IR Spectroscopy. Except for **5**, all trinuclear complexes show an integral proton ratio of bidentate ligands of peripheral units to that of phen ligand of central unit of 2:1, confirming the coordination of two peripheral Re(I) complexes with both cyano ligands of the central bridging metalloligands, **P1** and **P2**. Although the two peripheral complex units in the crystal structures of **2**−**6** are unsymmetrical (see below), the bidentate ligands on these peripheral units only give rise to one set of ^{1}H NMR signals. This is due to the free rotation of the peripheral units in the solution state, while for **5**, since the peripheral complex moieties do not contain any proton, only one set of ^{1}H NMR signals for the phen ligand of the central unit, which is downfield-shifted compared to **P1**, is observed. The *cis,trans*- and *cis,cis*-isomerism of [Re(CO)$_2$(CN)$_2$(phen)]$^-$ of **P1** and **P2** or in the central bridging metalloligand unit of the trinuclear complexes can be readily distinguished by the symmetrical and unsymmetrical ^{1}H NMR signals of their phen ligand.

Scheme 2. Synthetic Routes for Trinuclear Re(I) Complexes 1−7



All trinuclear Re(I) complexes (**1**−**7**) exhibit 2−3 C≡O stretches and 1 or 2 active C≡N stretches in their IR spectra. For the monomeric complexes **M1**−**M3** with the general formula of [Re(PPh$_3$)(CO)$_2$(MeCN)(N−N)]$^+$, they can be characterized by two C≡O stretches. For complexes **1**−**7**, these complexes display C≡N stretches of bridging cyanide ligands in the range of 2083−2130 cm^{-1}, which are ca. 22−34 cm^{-1} higher than those of the terminal cyanides of **P1** and **P2**. This is due to the kinematic coupling, where the CN motion is constrained by the presence of the second metal center,[23] that leads to higher stretching frequency of the bridging cyanide ligands.[24] Concerning the C≡O stretches in the trinuclear complexes, the carbonyl ligands in each Re(I) complex moiety should exhibit 2 or 3 IR active stretches; therefore, the trinuclear complexes are expected to show a number of C≡O stretches. However, only two to three board IR stretches at 1844−2039 cm^{-1} were observed in their IR spectra. This is probably due to the significant overlapping of the IR active C≡O stretches as the stretching frequencies of these carbonyl ligands are expected to be similar. In addition, the hexafluorophosphate (PF$_6^-$) anions in **1**−**5** are characterized by ν(P−F) at 841−843 cm^{-1}.

X-ray Crystal Structure Determination. The crystal structures of trinuclear complexes **2**−**6** were determined by X-ray crystallography. The perspective drawings of the complex cations with atomic numbering are displayed in Figure 1. The crystal and structure determination data are tabulated in Table S1, while the selected bond angles and distances are collected in Table S2. As revealed from the crystal structures, trinuclear complexes **2**−**6** show considerable variation in the relative orientation of the peripheral units to the central Re(I) moiety. With reference to the plane of the bidentate ligand and two carbonyl ligands of central unit, the orientation of the central unit of **2** is rotated 90 and 180° relative to the two peripheral moieties, and the orientations of the two symmetrical peripheral moieties are related by a 90° rotation. For **3**, the orientation of central unit is 90° relative to both peripheral moieties, and the two symmetrical peripheral moieties are in the same ligand orientation. For **4**, the orientation of central unit is rotated 90 and 0° relative to the two peripheral moieties, and the orientations of the two symmetrical peripheral moieties are related by a 90° rotation. For **5**, the orientation of the two symmetrical peripheral moieties is related by a ca. 20° rotation. For **6**, the orientation of central unit is ca. 90° relative to both peripheral moieties, and the orientations of the two symmetrical peripheral moieties are related by a 180° rotation.

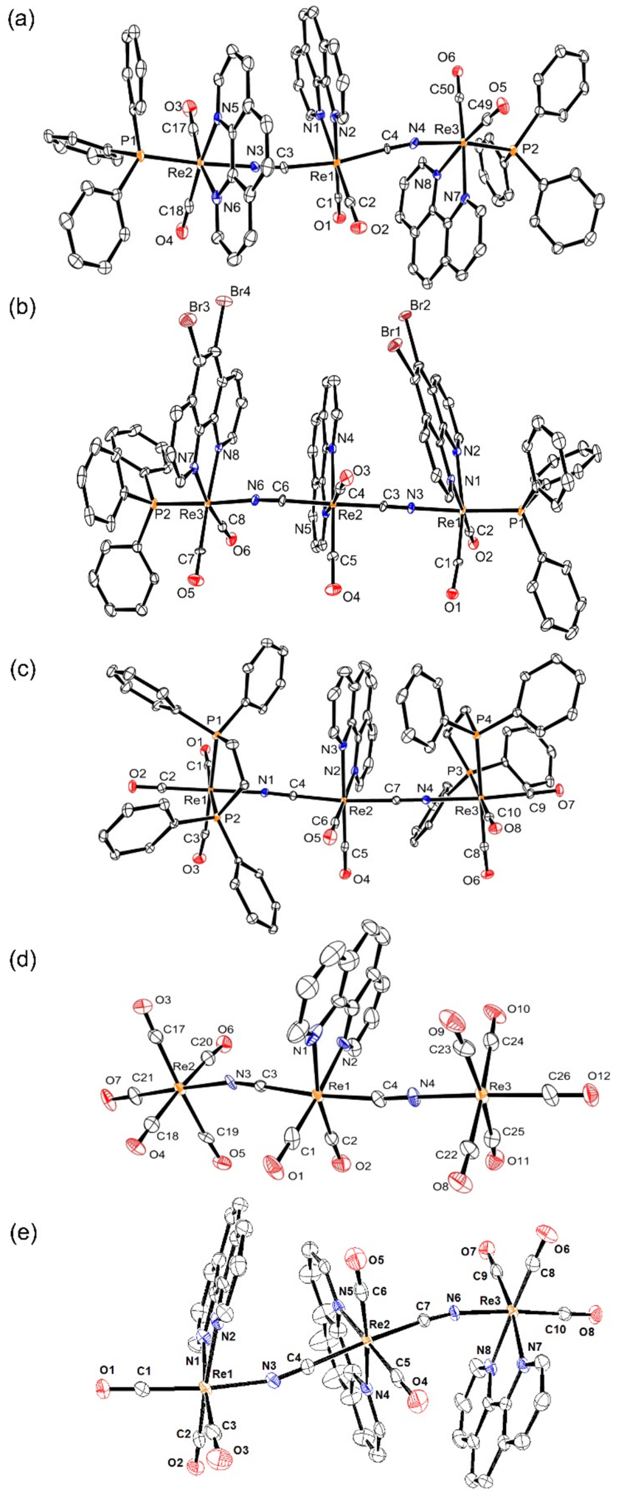


Figure 1. Perspective drawing of the complex cation of (a) **2**, (b) **3**, (c) **4**, (d) **5**, and (e) **6** with the atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Except for **5**, the rhenium metal centers of all these structures adopted a distorted octahedral geometry as a result of steric requirements of the bidentate ligands. The values of the bite angles of the bidentate diimine and diphosphine ligands are in the ranges of 74.8−76.3° and 80.6−81.7°, respectively, which are common in other related rhenium complexes bearing diimine and diphosphine ligands.[25] Owing to the lower rigidity of the diphosphine ligand relative to that of other diimine ligands, the bite angle of diphosphine ligand in **4** is larger compared to those of the diimine ligands in other structures. The bending of cyanides in Re−CN−Re (averaged bond angles of C≡N−Re and Re−C≡N) are in the range of 171.9−175.3°. This slight bending can be attributed to the π-back-bonding interactions of cyanide ligands with both the peripheral and central rhenium centers. The bond lengths of C≡N, Re−CN, and Re−CO, in the ranges of 1.12−1.16 Å, 2.07−2.10 Å, and 1.88−2.05 Å, respectively, are in the typical ranges reported in tricarbonyl rhenium and cyano rhenium complexes.[18,19,25b,c]

UV−Vis Spectroscopy. The electronic absorption properties of complexes **1**−**7** and **M1**−**M3** in CH_2Cl_2 solution have been investigated. Their UV−vis absorption spectra are shown in Figure 2, and the absorption data are summarized in Table 1. All of these complexes exhibit intense absorption, corresponding to the spin allowed intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the PPh_3 and/or diimine moieties, in the UV region of 248−381 nm with molar extinction coefficients on the order of 10^4 dm^3 mol^{-1} cm^{-1}. Apart from the ligand-centered transitions, an additional moderately intense absorption band ($\varepsilon > 10^3$ dm^3 mol^{-1} cm^{-1}) was found in the lower energy visible region in the absorption spectra. With reference to the spectroscopic studies of related Re(I) complexes,[26] this lowest-energy absorption band, with absorption maxima ranging from 405 to 475 nm, is assigned to the ^{3}MLCT [dπ(Re) → π^*(N−N)] transitions. For trinuclear complexes **1**−**3**, **6**, and **7**, owing to the similar transition energy of MLCT [dπ(Re) → π^*(N−N)] chromophores in both peripheral and central units, the lowest-energy absorption band is assigned as a mixture of two different MLCT [dπ(Re) → π^*(N−N)] transitions. Consequently, the absorption maxima of each type of MLCT transitions are difficult to determine accurately. Furthermore, the broader absorption bands, together with the almost doubled extinction coefficient of **1**−**3** in comparison with those of corresponding mononuclear complexes (**M1**−**M3**; Figure 2a), are supportive of the assignment of admixture of the MLCT transitions from peripheral and central Re(I)

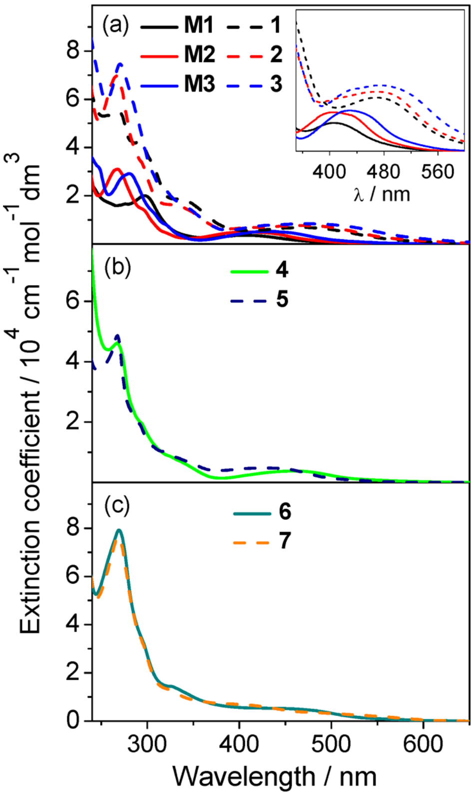


Figure 2. Overlaid UV−vis absorption spectra of (a) **M1**−**M3** and **1**−**3**, (b) **4** and **5**, and (c) **6** and **7** in dichloromethane solution at 298 K.

Table 1. UV−Vis Absorption Data for 1−7 and M1−M3

complex	absorption, λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})
1	269 (54790), 292 (42470), 340 (18300), 469 (6820)
2	267 (69760), 295 sh (33045), 336 (15500), 470 (7575)
3	271(74610), 320 sh (22235), 344 sh (15025), 475 (8380)
4	268 (46170), 294 sh (19615), 333 sh (7250), 459 (3785)
5	268 (48650), 292 sh (19240), 319 sh (10230), 427 (4825)
6	267 (84200), 284 sh (44555), 313 sh (16085), 446 (5380)
7	267 (76385), 284 sh (42085), 312 sh (14885), 381 sh (7130), 471 (3610)
M1	259 sh (16985), 275 (16560), 297 (20000), 405 (3590)
M2	267 (31015), 296 sh (14170), 321 sh (4360), 407 (4930)
M3	248 sh (31410), 281 (29160),305 sh (13760), 322 sh (7785), 431 (5160)

moieties. As the peripheral units in trinuclear complexes **4** and **5** do not possess any π-accepting diimine ligands, the extinction coefficient of their lowest energy MLCT [dπ(Re) → π*(phen)] absorption bands resembles that of *cis,trans*-$[Re(CO)_2(CN)_2(phen)]^-$.[18] The MLCT absorption energy of **5** (427 nm) is higher than that of **4** (459 nm) (Figure 2b). This can be explained by the stronger electron-withdrawing peripheral rhenium moieties $[Re(CO)_5]^+$ in **5**, which render the dπ(Re) orbital of central Re(I) unit more stabilized and thus lead to a higher MLCT energy. The MLCT assignment is consistent with the DFT calculations on selected complexes (**2**, **5**, and **6**), in which their HOMOs are mainly dπ(Re) orbital in character and LUMOs are π* orbital of the phenanthroline ligands (Table S3). Concerning the effect of the *trans* and *cis* configurations of the two cyanide bridging ligands of the central metalloligand, no obvious difference is noted between the electronic absorption properties of complexes **6** and **7** (Figure 2c).

For mononuclear complexes **M1**−**M3**, the lowest MLCT [dπ(Re) → π*(N−N)] absorption energy decreases on passing from a weaker π-accepting diimine ligand to a stronger one, as reflected by the absorption maxima trend: **M1** (405 nm) < **M2** (407 nm) < **M3** (431 nm). This can be rationalized by the lower-lying π* orbital in the better π-accepting diimine ligand, which therefore gives rise to a smaller MLCT energy gap.

Emission Spectroscopy. With the exception of trinuclear complex **3**, all Re(I) complexes **1**−**7** and **M1**−**M3** display orange to red luminescence in CH_2Cl_2 solution at room temperature upon photoexcitation (λ ≥ 350 nm). The emission maxima of mononuclear complexes **M1**−**M3** are in the region of 618−660 nm, whereas those of trinuclear complexes **1**, **2**, and **4**−**7** (Figure 3) are in the range of 650−752 nm (Table 2).

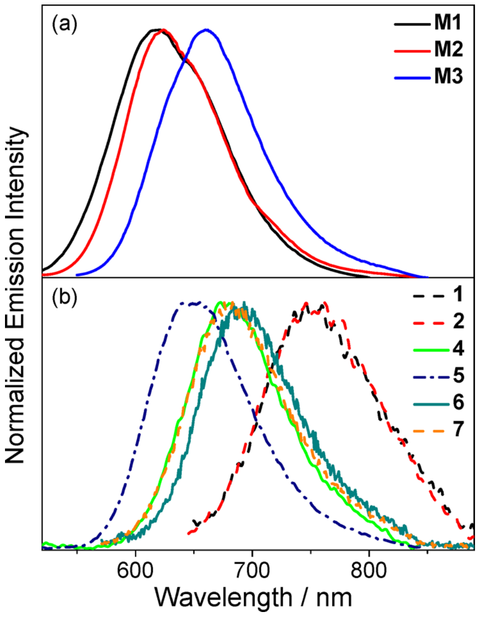


Figure 3. Overlaid normalized emission spectra of (a) mononuclear complexes and (b) trinuclear Re(I) complexes in CH_2Cl_2 solution at 298 K.

For the mononuclear complexes, the emission energy [**M1** (618 nm) > **M2** (625 nm) > **M3** (660 nm)] (Figure 3a) is inversely related to the π-accepting ability of the diimine ligands: Br_2phen > phen > Me_2bpy. On the basis of the sensitivity of emission energy to the electronic properties of the diimine ligands as well as previous spectroscopic studies, these emissions are assigned to be derived from the ^{3}MLCT [dπ(Re) → π*(N−N)] excited state. The lower MLCT emission energy in complexes with better π-accepting diimine ligands can be attributed to the smaller MLCT energy gap as a result of the lower-lying π*(N−N) orbital.

With reference to previous spectroscopic studies on related Re(I) phenanthroline complexes,[18,27] the emissions of trinuclear complexes **4** and **5** (Figure 3b) are assigned as MLCT [dπ(Re) → π*(phen)] phosphorescence. Due to the nonemissive behavior of the peripheral rhenium moieties in **4** and **5**, these emissions are ascribed to that of the central Re(I) luminophore. The emission of **5** (650 nm) is blue-shifted as

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Table 2. Emission Data for 1−7 and M1−M3

complex	medium (T/K)	emission, λ_{em}/nm (τ_o/μs)	quantum yield, $\Phi_{em} \times 10^{2a}$
1	CH_2Cl_2 (298)	752 (0.066)	0.30
	glass (77)^b	625 (0.67)	
2	CH_2Cl_2 (298)	752 (0.056)	0.71
	glass (77)^b	635 (0.757)	
3	CH_2Cl_2 (298)	c	c
	glass (77)^b		
4	CH_2Cl_2 (298)	679 (0.044)	1.32
	glass^b (77)	600 (1.29)	
5	CH_2Cl_2 (298)	650 (0.101)	7.32
	glass (77)^b	590 (1.65)	
6	CH_2Cl_2 (298)	696 (0.024)	0.78
	glass^b (77)	612 (1.09)	
7	CH_2Cl_2 (298)	681 (0.053)	0.91
	glass (77)^b	615 (2.26)	
M1	CH_2Cl_2 (298)	618 (0.043)	3.04
	glass (77)^b	553 (2.71)	
M2	CH_2Cl_2 (298)	625 (0.105)	5.40
	glass (77)^b	556 (6.31)	
M3	CH_2Cl_2 (298)	660 (0.075)	4.11
	glass (77)^b	580 (3.29)	

[a] Measured with 436 nm excitation using $[Ru(bpy)_3]Cl_2$ as the reference. [b] EtOH/MeOH = 4:1 (v/v). [c] Nonemissive or not detectable.

compared to that of **4** (679 nm). The higher emission energy in **5** with the stronger electron-withdrawing peripheral rhenium moieties $[Re(CO)_5]^+$ is consistent with the MLCT [dπ(Re) → π*(phen)] excited state assignment, while for trinuclear complexes **1**, **2**, **6**, and **7**, which consist of two different MLCT luminophores, the emissions are also assigned to be derived from the ^{3}MLCT [dπ(Re) → π*(phen)] excited state of the central luminophore. The assignment was done based on the following considerations: (1) significant red-shifted emission energies relative to that of corresponding mononuclear analogues [**1** (~752 nm) vs **M1** (~618 nm); **2** (~752 nm) vs **M2** (~625 nm); **6** (~696 nm) and **7** (~681 nm) vs $[Re(CO)_3(phen)(MeCN)]^+$ (532 nm)];[28] (2) insensitivity of emission maxima to the change in diimine ligands [**1** (~752 nm) ≈ **2** (~752 nm)] on the peripheral units; (3) sensitivity of the geometrical isomerism of **6** and **7**; and (4) lower emission energies than that of **5** (Figure 3), which is in line with the weaker electron-withdrawing peripheral Re(I) complex units. In contrast to other trinuclear complexes, the solution of **3** at room temperature is nonemissive or very weakly emissive, which is not detectable. Compared to **1** and **2**, which show weak and low-energy emission in the NIR region (peaking at 752 nm), the presence of the electron-withdrawing bromo substituents in **3** would render the ^{3}MLCT state lower in energy, resulting in more efficient nonradiative thermal deactivation.

These complexes also emit in EtOH/MeOH (4:1 v/v) glassy medium at 77 K. These emissions are blue-shifted relative to those of the solution state due to the "luminescence rigidochromism", which is typically found in other related systems (Table 2, Figure S1).[29] On the basis of the similar emission energy trend, the emissions of trinuclear complexes **1**, **2**, and **4**−**7** at 77 K are also assigned as MLCT [dπ(Re) → π*(phen)] phosphorescence of the central unit. Although some of these trinuclear Re(I) complexes contain more than one Re(I) luminophore, only the MLCT phosphorescence of the central unit with the lowest MLCT energy is observed in the solution state at room temperature as well as in the glassy state at low temperature. This suggests that the intramolecular energy transfer processes between different Re(I) luminophores are very efficient (Figure 4). The lower MLCT energy of the central luminophore compared to those of peripheral luminophores has also been confirmed by DFT calculations (Figures 5 and S2, Table S3). Likewise, the emissions of the mononuclear components are also assigned as derived from the ^{3}MLCT [dπ(Re) → π*(N−N)] excited state origin. The observed emission lifetimes in the microsecond range further support the phosphorescence assignment.

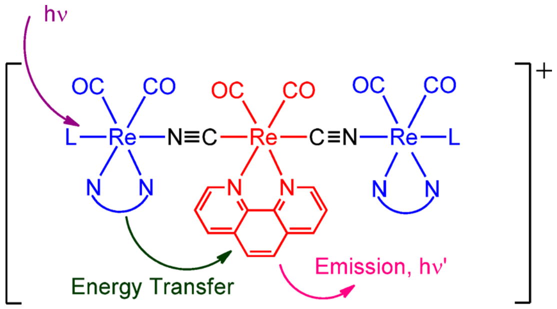

Figure 4. Schematic diagram showing the energy transfer process between different MLCT luminophores.

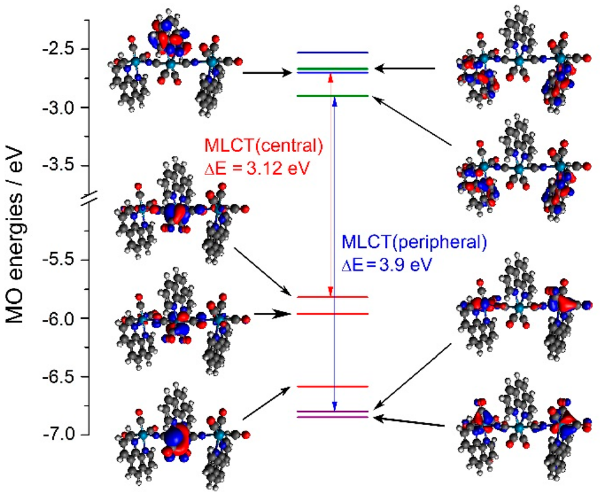

Figure 5. Computed MO energies and the contour surfaces of HOMO−4 to LUMO+3 of **6**.

Electrochemistry. The electrochemical properties of trinuclear Re(I) complexes **1**−**7** were studied by cyclic voltammetry in acetonitrile (0.1 mol dm^{-3} in $^nBu_4NPF_6$). Except for **5**, all trinuclear Re(I) complexes **1**−**7** display three quasi-reversible oxidation couples (Table 3). The representative cyclic voltammograms of **6** are shown in Figure 6. To gain insight into these oxidation processes, controlled-potential coulometry of **6** by electrolysis at potentials (+0.1 V above each oxidative wave) was performed, which showed that each oxidation is a one-electron process. With reference to previous electrochemical study,[26a,30] all the Re(I) complex analogues would undergo irreversible or quasi-reversible metal-centered Re(I/II) oxidation at similar potentials. Therefore, these

Table 3. Electrochemical Data for 1−7 and M1−M3 in CH_3CN Solution (0.1 M $^{n}Bu_4NPF_6$) at 298 K[a]

complex	oxidation [$E_{1/2}$/V vs SCE (E_{pa}/V vs SCE)][b]	reduction [$E_{1/2}$/V vs SCE (E_{pc}/V vs SCE)][b]
1	0.71, 0.97, 1.19	(−1.68)[c,d]
2	0.68, 0.92, 1.17	−1.52[d]
3	0.73, 1.01, 1.25	(−1.21)[c,d]
4	0.87, 1.54, (2.09)[c]	−1.54
5	0.92, (1.75)[c]	(−1.42)[c,d]
6	0.90, 1.39, 1.75	−1.30[d]
7	0.83, 1.41, 1.74	−1.33[d]
P1	0.43	−1.64
M1	1.17	(−1.60),[c] (−1.80),[c] (−2.20)[c]
M2	1.20	(−1.42),[c] (−1.61),[c] (−1.97)[c]
M3	1.23	(−1.29)[e]

[a] Working electrode, glassy carbon; scan rate, 100 mVs^{-1}. [b] $E_{1/2}$ is $(E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively. [c] Irreversible wave. [d] Reduction potentials at more cathodic region were not determined due to the significant mixing and overlapping of reductions of various moieties, including the ligand-based reductions and metal-centered reductions of the peripheral and central rhenium moieties. [e] Only one irreversible reduction wave was determined, as it shows significant decomposition on scanning to more negative potential.

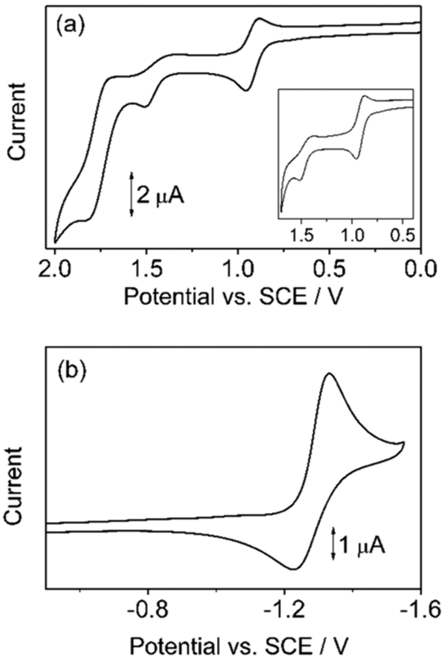

Figure 6. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of **6** in MeCN (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$). Scan rate: 100 mVs^{-1}.

oxidations were assigned as metal-centered Re(I/II) oxidations. As the Re(I) metal center of the central moiety is more electron-rich than those of the peripheral one, the first oxidation couple is assigned to the Re(I/II) metal-centered oxidation of the central moiety. Compared to Re(I/II) metal-centered oxidation of **P1**, the oxidation potentials of the central unit in these trinuclear complexes show an anodic shift, consistent with the decrease of electron richness upon coordination to two cationic peripheral coordination unit. The two oxidation couples at more anodic potentials are attributable to the successive Re(I/II) metal-centered oxidations of the two peripheral rhenium units. These assignments are further supported by the higher sensitivity of the second and third oxidation potentials to the change in bidentate and the ancillary ligands on peripheral units. The splitting of the peripheral metal-centered oxidation potentials of ca. 0.2−0.3 V was observed, suggesting significant metal−metal electronic communication through the N≡C−Re−C≡N bridge. The 200−300 mV difference between the two oxidation potentials is comparable to that of many related trimetallic cyano-bridged complexes with effective electronic mixing.[14c,17]

In the reductive scan, due to the significant mixing and overlapping of reductions from different moieties in trinuclear complexes **1**−**7**, only the first reduction potential was determined. This reduction is ascribed to the diimine ligand-based reduction (the peripheral complex moiety for **1**−**3**, **6**, and **7** and the central complex unit for **4** and **5**), as commonly found in other Re(I) diimine complexes.[26,27]

■ CONCLUSION

The first series of cyano-bridged homotrinuclear Re(I) complexes and their corresponding mononuclear analogues have been synthesized. The structures of most of the trinuclear complexes have been characterized by X-ray crystallography and show different relative orientations of the peripheral to the central Re(I) units. With the exception of **3**, which is nonemissive, all trinuclear Re(I) complexes exhibit orange to red MLCT [dπ(Re) → π*(N−N)] phosphorescence in dichloromethane solution at room temperature and in 77 K glassy medium. This is ascribed to the ^{3}MLCT [dπ(Re) → π*(phen)] excited state origin of the central Re(I) unit. The observation of the phosphorescence from the central Re(I) luminophore is suggestive of efficient energy transfer process between the peripheral and central Re(I) units. Detailed electrochemical studies on these complexes revealed that all trinuclear complexes generally exhibit three oxidation couples and/or waves. The first oxidation couple is ascribed to the oxidation of Re(I) to Re(II) of the central unit, whereas the remaining two oxidation peaks are corresponding to the Re(I/II) oxidation of the two peripheral units. The splitting of the two oxidation waves of the chemically equivalent peripheral rhenium metal centers with $\Delta E_{1/2} \approx 0.2$−$0.3$ V clearly demonstrated the significant intermetallic electronic communication across the [NC−Re−CN] bridge in these complexes. In short, the present study should also offer insights into the electronic and luminescent properties of the dicyanorhenate metalloligands and their trinuclear Re(I) complexes. It also enables the development of Re(I)-based molecular wires and networks with designed properties.

■ EXPERIMENTAL SECTION

Materials and Reagents. 1,10-Phenanthroline monohydrate (phen), 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy), triphenylphosphine (PPh_3), silver trifluoromethanesulfonate (AgOTf), and $[Re_2(CO)_{10}]$ were purchased from Strem Chemicals Company and used without further purification. Trimethyl amine *N*-oxide dihydrate ($Me_3NO \cdot 2H_2O$) and 1,2-bis(diphenylphosphino)ethane (dppe) were obtained from Aldrich Chemical Co. $[Re(CO)_5Br]$ was synthesized from the reaction between $[Re_2(CO)_{10}]$ and bromine according to a literature procedure.[22] 5,6-Dibromo-1,10-phenanthroline (Br_2phen) was prepared according to previously published procedure.[31] *cis,trans*-($^{n}Bu_4N$)[Re(CO)$_2$(CN)$_2$(phen)] (**P1**),[22] *fac*-[Re(CO)$_3$(Me$_2$bpy)-Br],[30a] *fac*-[Re(CO)$_3$(phen)Br],[30a] *fac*-[Re(CO)$_3$(dppe)Br],[21] and *fac*-[Re(CO)$_3$(phen)(PPh$_3$)](CF$_3$SO$_3$)[32] were prepared according to literature procedures with slight modifications. All solvents were of analytical reagent grade and were used without further purification. The synthetic routes for the target trinuclear complexes are summarized in Scheme 1. Unless specified in the procedure, all the reactions were performed under anhydrous conditions and strictly inert argon atmosphere using standard Schlenk techniques.

***cis,cis*-K[Re(CO)$_2$(CN)$_2$(phen)] (P2).** The title complex was prepared from the reaction of *fac*-[Re(CO)$_3$(phen)(CN)] (50 mg, 0.10 mmol) with KCN (650 mg, 10 mmol) in degassed MeOH/H$_2$O solution (6:1 v/v) (20 mL). After UV irradiation (λ = 254 nm) for 7 h at room temperature, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone/methanol (5:5:1 v/v/v) as eluent. Yield: 14 mg, 0.03 mmol; 26%. ^{1}H NMR (400 MHz, CD$_3$OD, 298 K): δ 7.78 (dd, 1H, J = 5.2, 8.2 Hz, 3-phen H's), 7.96 (dd, 1H, J = 5.2, 8.2 Hz, 8-phen H's), 8.11 (d, 2H, J = 0.9 Hz, 5,6-phen H's), 8.55 (dd, 1H, J = 1.4, 8.2 Hz, 4-phen H's), 8.68 (dd, 1H, J = 1.4, 8.2 Hz, 7-phen H's), 9.64 (dd, 1H, J = 1.4, 5.2 Hz, 2-phen H's), 9.81 (dd, 1H, J = 1.4, 5.1 Hz, 9-phen's). ESI-MS: m/z 475 [M]$^-$. IR (KBr disc, ν/cm^{-1}) 1827, 1905 ν(C≡O), 2061, 2096 ν(C≡N). Elemental analyses: Calcd for **P2** (found) %: C 37.42 (37.35), H 1.57 (1.76), N 10.91 (10.89).

***fac*-[Re(CO)$_3$(Br$_2$phen)Br].** Re(CO)$_5$Br (500 mg, 1.23 mmol) was mixed with Br$_2$phen (500 mg, 1.48 mmol, 1.2 mol equiv) in benzene/THF solution (1:1 v/v, 30 mL) and heated to reflux for 1 night. After removal of the solvent under reduced pressure, the residue was washed with petroleum ether. Yield: 331 mg, 0.98 mmol; 80%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.97 (dd, 2H, J = 5.1, 8.6 Hz, 3,8-phen H's), 9.02 (dd, 2H, J = 8.5, 1.3 Hz, 4,7-phen H's), 9.47 (dd, 2H, J = 5.2, 1.2 Hz, 2,9-phen H's). IR (KBr disc, ν/cm^{-1}) 1900, 1938, 2024 ν(C≡O). Elemental analyses: Calcd for *fac*-[Re(CO)$_3$(Br$_2$phen)Br] (found) %: C 26.18 (25.90), H 0.88 (1.01), N 4.07 (4.28).

***fac*-[Re(CO)$_3$(Me$_2$bpy)(PPh$_3$)](CF$_3$SO$_3$).** A mixture of *fac*-[Re(CO)$_3$(Me$_2$bpy)Br] (250 mg, 0.47 mmol) and AgOTf (144 mg, 0.56 mmol, 1.2 mol equiv) was refluxed in THF solution for 2 h. The resulting suspension was filtered to remove the precipitated AgBr. Excess triphenylphosphine ligand (981 mg, 3.76 mmol, 8 mol equiv) was added, and the reaction was heated to reflux overnight. Subsequent removal of solvent under reduced pressure and purification by column chromatography on silica gel using dichloromethane/acetone (3:1 v/v) as eluent gave analytically pure product. Yield: 333 mg, 0.39 mmol; 82%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 2.63 (s, 6H, methyl H's), 6.95 (d, 2H, J = 5.8 Hz, 5,5′-bpy H's), 7.13−7.18 (m, 6H, phenyl H of PPh$_3$), 7.28−7.33 (m, 6H, phenyl H of PPh$_3$), 7.37−7.41 (m, 3H, phenyl H of PPh$_3$), 8.14 (d, 2H, J = 5.8 Hz, 6,6′-bpy H's), 8.79 (s, 2H, 3,3′-bpy H's). ESI-MS: m/z 718 [M]$^+$. IR (KBr disc, ν/cm^{-1}) 1920, 1960, 2039 ν(C≡O). Elemental analyses: Calcd for *fac*-[Re(CO)$_3$(Me$_2$bpy)(PPh$_3$)]CF$_3$SO$_3$·CH$_2$Cl$_2$ (found) %: C 44.21 (44.01), H 3.07 (3.23), N 2.95 (2.73).

***fac*-[Re(CO)$_3$(Br$_2$phen)(PPh$_3$)](CF$_3$SO$_3$).** The complex was synthesized according to a procedure similar to that for *fac*-[Re(CO)$_3$(Me$_2$bpy)(PPh$_3$)](CF$_3$SO$_3$) except that *fac*-[Re(CO)$_3$(Br$_2$phen)Br] (323 mg, 0.47 mmol) was used in place of *fac*-[Re(CO)$_3$(Me$_2$bpy)Br]. Yield: 407 mg, 0.40 mmol; 85%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 6.98−7.02 (m, 6H, phenyl H of PPh$_3$), 7.22−7.26 (m, 6H, phenyl H of PPh$_3$), 7.35−7.38 (m, 3H, phenyl H of PPh$_3$), 8.04 (dd, J = 5.2, 8.6 Hz,2H, 3,8-Br$_2$phen H's), 9.01 (d, 2H, J = 8.5 Hz, 4,7-phenH's), 9.17 (d, 2H, J = 5.4 Hz, 2,9-phen H's). ESI-MS: m/z 1013 [M]$^+$. IR (KBr disc, ν/cm^{-1}) 1919, 1961, 2040 ν(C≡O). Elemental analyses: Calcd for *fac*-[Re(CO)$_3$(Br$_2$phen)(PPh$_3$)]CF$_3$SO$_3$ (found) %: C 40.05 (40.26), H 2.08 (2.28), N 2.75 (2.51).

***cis,trans*-[Re(CO)$_2$(PPh$_3$)(Me$_2$bpy)(MeCN)](CF$_3$SO$_3$) (M1).** A solution of *fac*-[Re(CO)$_3$(Me$_2$bpy)(PPh$_3$)]CF$_3$SO$_3$ (150 mg, 0.18 mmol) and Me$_3$NO·2H$_2$O (24 mg, 0.21 mmol, 1.2 mol equiv) in acetonitrile solution was warmed at ca. 80 °C overnight. The residue was purified by column chromatography on silica gel using dichloromethane/methanol (20:1 v/v) as eluent. Yield: 110 mg, 0.10 m.mol; 70%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 2.24 (s, 3H, MeCN), 2.67 (s, 6H, methyl H's), 6.87 (d, 2H, J = 5.8 Hz, 5,5′-bpy H's), 7.17−7.23 (m, 13H, phenyl H of PPh$_3$), 7.26−7.29 (m, 2H, phenyl H of PPh$_3$), 8.12 (d, J = 5.7 Hz, 6,6′-bpy H's), 8.52 (s, 2H, 3,3′-bpy H's). ESI-MS: m/z 728 [M]$^+$. IR (KBr disc, ν/cm^{-1}) 1867, 1939 ν(C≡O). Elemental analyses: Calcd for **M1**·CH$_3$OH (found) %: C 47.47 (47.77), H 3.76 (3.93), N 4.61 (4.74).

***cis,trans*-[Re(CO)$_2$(phen)(PPh$_3$)(MeCN)]CF$_3$SO$_3$ (M2).** The title compound was synthesized according to a previously published procedure.[23]

***cis,trans*-[Re(CO)$_2$(Br$_2$phen)(PPh$_3$)(MeCN)](CF$_3$SO$_3$) (M3).** The complex was synthesized according to a procedure similar to that for **M1** except that *fac*-[Re(CO)$_3$(Br$_2$phen)(PPh$_3$)](CF$_3$SO$_3$) (183 mg, 0.18 mmol) was used in place of *fac*-[Re(CO)$_3$(Me$_2$bpy)(PPh$_3$)]-(CF$_3$SO$_3$). Yield: 111 mg, 0.11 mmol; 60%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 2.13 (s, 3H, MeCN), 6.95−7.00 (m, 6H, phenyl H of PPh$_3$), 7.03−7.07 (m, 6H, phenyl H of PPh$_3$), 7.13−7.15 (m, 3H, phenyl H of PPh$_3$), 7.54 (dd, 2H, J = 8.6, 5.2 Hz, 3,8-phenyl H's), 8.77 (dd, 2H, J = 8.6, 1.2 Hz, 4,7-phenyl H's), 8.80 (d, 2H, J = 5.1 Hz, 2,9-phenyl H's). ESI-MS: m/z 882 [M]$^+$. IR (KBr disc, ν/cm^{-1}) 1869, 1941 ν(C≡O). Elemental analyses: Calcd for **M3**·CHCl$_3$ (found) %: C 37.53 (37.73), H 2.19 (2.33), N 3.65 (3.81).

[(PPh$_3$)(Me$_2$bpy)(CO)$_2$Re(μ-CN)Re(CO)$_2$(phen)(μ-CN)Re(CO)$_2$(Me$_2$bpy)(PPh$_3$)](PF$_6$) (1). A solution of **M1** (50 mg, 0.057 mmol) and **P1** (17 mg, 0.025 mmol, 0.43 mol equiv) in THF/methanol (20:1 v/v, 60 mL) was warmed overnight at 50 °C. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using dichloromethane/methanol (20:1 v/v) as eluent. Subsequent metathesis reaction with a saturated methanolic ammonium hexafluorophosphate solution gave the target complex as a PF$_6^-$ salt. The complex was further purified by slowly diffusing diethyl ether vapor into a concentrated dichloromethane/chloroform (20:1 v/v) solution of **1** to yield red crystalline solid. Yield: 33 mg, 0.017 mmol; 68%. ^{1}H NMR (400 MHz, CD$_3$CN, 298 K): δ 2.36 (s, 12H, methyl H's), 6.61 (d, 4H, J = 5.7 Hz, 5,5′-bpy H's), 6.99−7.03 (m, 12H, phenyl H of PPh$_3$), 7.12−7.08 (m, 12H, phenyl H of PPh$_3$), 7.16−7.20 (m, 10H, 3,3′-bpy H's and phenyl H of PPh$_3$), 7.46 (dd, 2H, J = 5.1, 8.2 Hz, 3,8-phen H's), 7.78 (d, 4H, J = 5.7 Hz, 6,6′-bpy H's), 8.04 (s, 2H, 5,6-phen H's), 8.40 (d, 2H, J = 8.2 Hz, 4,7-phen H's), 8.56 (d, 2H, J = 5.1 Hz, 2,9-phenH's). ESI-MS: m/z 1852 [M]$^+$. IR (KBr disc, ν/cm^{-1}) 842 ν(P−F), 1844, 1923 ν(C≡O), 2093 ν(C≡N). Elemental analyses: Calcd for **1**·0.5 CHCl$_3$ (found) %: C 46.87 (46.81), H 3.35 (3.13), N 5.43 (5.20).

[(PPh$_3$)(phen)(CO)$_2$Re(μ-CN)Re(CO)$_2$(phen)(μ-CN)Re(CO)$_2$(phen)(PPh$_3$)](PF$_6$) (2). The title complex was synthesized according to a procedure similar to that for **1** except that **M2** (50 mg, 0.057 mmol) was used in place of **M1** in the substitution reaction. Red crystals of **2** were obtained by slow diffusion of diethyl ether vapor into a concentrated dichloromethane/chloroform (5:1 v/v) solution of **2**. Yield: 32 mg, 0.016 mmol; 62%. ^{1}H NMR (400 MHz, CD$_3$CN, 298 K): δ 6.84−6.88 (m, 12H, phenyl H of PPh$_3$), 6.97−7.02 (m, 12H, phenyl H of PPh$_3$), 7.08−7.13 (m, 10H, 3,8-phen$_{\text{peripheral}}$ H's and phenyl H of PPh$_3$), 7.20 (dd, 2H, J = 5.1, 8.1 Hz, 3,8-phen$_{\text{central}}$ H's), 7.67 (s, 4H, 5,6-phen$_{\text{peripheral}}$ H's), 7.82 (s, 2H, 5,6-phen$_{\text{central}}$ H's), 8.07 (d, 4H, J = 8.2 Hz, 4,7-phen$_{\text{peripheral}}$ H's), 8.12 (d, 2H, J = 5.0 Hz, 4,7-phen$_{\text{central}}$ H's), 8.17 (d, 2H, J = 5.0 Hz, 2,9-phen$_{\text{central}}$ H's), 8.30 (d, 4H, J = 5.3 Hz, 2,9-phen$_{\text{peripheral}}$ H's). ESI-MS: m/z 1844 [M]$^+$. IR (KBr disc, ν/cm^{-1}) 842 ν(P−F), 1846, 1925 ν(C≡O), 2087 ν(C≡N). Elemental analyses: Calcd for **2**·0.5CHCl$_3$ (found) %: C 47.06 (47.35), H 2.97 (2.48), N 5.45 (5.64).

[(PPh$_3$)(Br$_2$phen)(CO)$_2$Re(μ-CN)Re(CO)$_2$(phen)(μ-CN)Re(CO)$_2$(Br$_2$phen)(PPh$_3$)](PF$_6$) (3). The title complex was synthesized according to a procedure similar to that for **1** except that **M3** (59 mg, 0.057 mmol) was used in place of **M1** in the substitution reaction. Column chromatography on silica gel using dichloromethane/acetone (3:1 v/v) as eluent gave **3** as red crystalline solid. Yield: 40 mg, 0.018 mmol; 70%. ^{1}H NMR (400 MHz, CD$_3$CN, 298 K): δ 6.85−6.90 (m, 12H, phenyl H of PPh$_3$), 6.98−7.02 (m,12H, phenyl H of PPh$_3$), 7.10−7.14 (m, 6H, phenyl H of PPh$_3$), 7.17−7.20 (m, 6H, 3,8-phen H's and 3,8-Br$_2$phen H's), 7.78 (s, 2H, 5,6-phen H's), 8.15 (d, 2H, J = 8.4 Hz, 4,7-phenH's), 8.23 (d, 2H, J = 5.4 Hz 2,9-phen H's), 8.37 (d, 4H, *J* = 8.4 Hz, 4,7-Br_2phen H's), 8.42 (d, 4H, *J* = 4.5 Hz, 2,9-Br_2phen H's). ESI-MS: *m/z* 2158 $[M]^+$. IR (KBr disc, ν/cm^{-1}) 843 ν(P−F), 1854, 1930 ν(C≡O), 2093 ν(C≡N). Elemental analyses: Calcd for **3**·CH_3CN (found) %: C 41.88 (41.53), H 2.53 (2.82), N 5.36 (4.98).

[(dppe)(CO)$_3$Re(μ-CN)Re(CO)$_2$(phen)(μ-CN)Re(CO)$_3$(dppe)](PF$_6$) (4). A mixture of [Re(CO)$_3$(dppe)Br] (60 mg, 0.08 mmol) and AgOTf (25 mg, 0.10 mmol, 1.2 mol equiv) in dichloromethane (30 mL) was stirred under argon at room temperature for 6 h. After filtration of the resulting suspension to remove the precipitated AgBr, **P1** (25 mg, 0.034 mmol, 0.43 mol equiv) dissolved in methanol was added. The reaction mixture was then warmed to 30 °C and stirred overnight. Subsequent metathesis reaction in methanol with a saturated methanolic solution of ammonium hexafluorophosphate afforded the target complex as a PF_6^- salt. Analytically pure red crystals were obtained from slow diffusion of diethyl ether vapor into a concentrated dichloromethane/ethanol solution of the complexes. Yield: 40 mg, 0.02 mmol; 60%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.79−1.89 (m, 4H, CH_2CH_2 H's), 2.33−2.53 (m, 4H, CH_2CH_2 H's), 7.08−7.14 (m, 10H, phenyl H of dppe), 7.29−7.82 (m, 32H, 3,8-phen H's and phenyl H of dppe), 7.95 (s, 2H, 5,6-phen H's), 8.14 (d, 2H, *J* = 5.0 Hz, 2,9-phen H's), 8.27 (d, 2H, *J* = 8.0 Hz, 4,7-phen H's). ESI-MS: *m/z* 1811 $[M]^+$. IR (KBr disc, ν/cm^{-1}) 841 ν(P−F), 1856, 1923, 2030 ν(C≡O), 2085 ν(C≡N). Elemental analyses: Calcd for **4**·C_2H_5OH (found) %: C 45.39 (45.64), H 3.51 (3.42), N 2.79 (3.07).

[(CO)$_5$Re(μ-CN)Re(CO)$_2$(phen)(μ-CN)Re(CO)$_5$](PF$_6$) (5). The title complex was synthesized according to a procedure similar to that for **4** except that [Re(CO)$_5$Br] (32 mg, 0.08 mmol) was used in place of [Re(CO)$_3$(dppe)Br] in the substitution reaction. Slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution gave **5** isolated as orange crystals. Yield: 25 mg, 0.02 mmol; 60%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.96 (dd, 2H, *J* = 5.1, 8.2 Hz, 3,8-phen H's), 8.18 (s, 2H, 5,6-phen H's), 8.73 (dd, 2H, *J* = 1.4, 8.3 Hz, 4,7-phen H's), 9.41 (dd, 2H, *J* = 1.3, 5.1 Hz, 2,9-phen H's). ESI-MS: *m/z* 1128 $[M]^+$. IR (KBr disc, ν/cm^{-1}) 843 ν(P−F), 1854, 1929, 2039 ν(C≡O), 2098 ν(C≡N). Elemental analyses: Calcd for **5** (found) %: C 24.32 (24.63), H 1.57 (1.27), N 4.36 (4.66).

***trans*-[(phen)(CO)$_3$Re(μ-CN)Re(CO)$_2$(phen)(μ-CN)Re(CO)$_3$(phen)](CF$_3$SO$_3$) (6).** **P1** (50 mg, 0.09 mmol) and *fac*-[Re(CO)$_3$(phen)(OTf)], prepared from the reaction of [Re(CO)$_3$(phen)Br] (112 mg, 0.21 mmol) and AgOTf (58 mg, 0.21 mmol), in 30 mL of methanol was vigorously stirred overnight at room temperature. After removal the solvent under reduced pressure, crystals of **6** were obtained from slow diffusion of diethyl ether into a concentrated chloroform/acetonitrile solution of **6**. Yield: 55 mg, 0.04 mmol; 37%. ^1H NMR (400 MHz, acetone-*d*, 298 K): δ 7.58 (dd, 2H, *J* = 5.0, 8.2 Hz, 3,8-$phen_{central}$ H's), 7.81 (dd, 4H, *J* = 5.1, 8.2 Hz, 3,8-$phen_{peripheral}$ H's), 8.12 (s, 4H, 5,6-$phen_{peripheral}$ H's), 8.26 (s, 2H, 5,6-$phen_{central}$ H's), 8.29 (dd, 2H, *J* = 1.3, 5.0 Hz, 4,7-$phen_{central}$ H's), 8.65 (dd, 2H, *J* = 1.3, 8.2 Hz, 2,9-$phen_{central}$ H's), 8.72 (dd, 4H, *J* = 1.3, 8.2 Hz, 4,7-$phen_{peripheral}$ H's), 8.99 (dd, 4H, *J* = 1.3, 5.1 Hz, 2,9-$phen_{peripheral}$ H's). ESI-MS: *m/z* 1375 $[M]^+$. IR (KBr disc, ν/cm^{-1}) 1850, 1918, 2024 ν(C≡O), 2092 ν(C≡N). Elemental analyses, Elemental analyses: Calcd for **6**·0.5$CHCl_3$ (found) %: C 36.65 (36.48), H 2.39 (2.18), N 6.91 (7.18).

***cis*-[(phen)(CO)$_3$Re(μ-CN)Re(CO)$_2$(phen)(μ-CN)Re(CO)$_3$(phen)](CF$_3$SO$_3$) (7).** The title complex was synthesized according to a procedure similar to that for **6** except that **P2** was used in place of **P1**. The crude product was purified by column chromatography on silica gel with $CHCl_3$/MeOH (9:1 v/v). Further purification by recrystallization from slowing diffusion of *n*-pentane into a concentrated chloroform solution of **7** gave pure complex as crystalline solid. Yield: 53 mg, 0.03 mmol; 36%. ^1H NMR (400 MHz, acetone-*d*, 298 K): δ 7.60 (dd, 1H, *J* = 2.9, 5.2 Hz, phen H's), 7.62 (dd, 1H, *J* = 2.9, 5.2 Hz, phen H's), 7.89 (dd, 1H, *J* = 5.1, 8.2 Hz, phen H's), 7.94 (dd, 1H, *J* = 5.1, 8.3 Hz, phen H's), 8.13 (dd, 1H, *J* = 1.4, 5.0 Hz, phen H's), 8.17 (d, 2H, *J* = 0.5 Hz, phen H's), 8.19 (d, 2H, *J* = 1.1 Hz, phen H's), 8.30 (dd, 1H, *J* = 4.3, 7.5 Hz, phen H's), 8.33 (dd, 1H, *J* = 4.2, 7.5 Hz, phen H's), 8.37 (d, 2H, *J* = 1.2 Hz, phen H's), 8.56 (dd, 1H, *J* = 1.4, 8.2 Hz, phen H's), 8.68 (dd, 1H, 1.4, 8.3 Hz, phen H's), 8.77 (dt, 2H, 1.4, 6.8 Hz, phen H's), 8.82 (dd, 1H, *J* = 1.4, 8.3 Hz, phen H's), 9.01 (dd, 1H, *J* = 1.3, 5.1 Hz, phen H's), 9.06−9.10 Hz, (m, 3H, phen H's), 9.67 (dd, 1H, 1.4, 5.1 Hz, phen H's), 9.71 (dd, 1H, *J* = 1.4, 5.1 Hz, phen H's). ESI-MS: *m/z* 1375 $[M]^+$. IR (KBr disc, ν/cm^{-1}) 1855, 1918, 2026 ν(C≡O), 2083, 2130 ν(C≡N). Elemental analyses: Calcd for **7**·$CHCl_3$ (found) %: C 35.71 (35.76), H 2.34 (2.02), N 6.66 (6.90).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00072.

> Experimental details for physical measurements and instrumentation, emission spectra of the complexes at 77 K EtOH/MeOH (4:1) glassy medium, calculated energies and the compositions of the frontier orbitals of **2**, **5**, and **6**, crystal and structure determination data, and selected bond lengths and bond angles (PDF)

Accession Codes

CCDC 1868105−1868109 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Selected examples: (a) Pfennig, B. W.; Fritchman, V. A.; Hayman, K. A. Synthesis, characterization, and photophysical properties of a series of supramolecular mixed-valence compounds. *Inorg. Chem.* **2001**, *40*, 255−263. (b) Kou, H.-Z.; Zhou, B. C.; Liao, D.-Z.; Wang, R.-J.; Li, Y. From one-dimensional chain to pentanuclear molecular. Magnetism of cyano-bridged Fe(III)-Ni(II) complexes. *Inorg. Chem.* **2002**, *41*, 6887−6891. (c) Wang, S.; Ding, X. H.; Zuo, J. L.; You, X. Z.; Huang, W. Tricyanometalate molecular chemistry: a type of versatile building blocks for the construction of cyano-bridged molecular architectures. *Coord. Chem. Rev.* **2011**, *255*, 1713−1732. (d) Alexandrov, E. V.; Virovets, A. V.; Blatov, V. A.; Peresypkina, E. V.

Topological motifs in cyanometallates: from building units to three-periodic frameworks. *Chem. Rev.* **2015**, *115*, 12286−12319.

(2) (a) Černák, J.; Orendáč, M.; Potočňák, I.; Chomič, J.; Orendáčová, A.; Skoršepa, J.; Feher, A. Cyanocomplexes with one-dimensional structures: preparations, crystal structures and magnetic properties. *Coord. Chem. Rev.* **2002**, *224*, 51−66. (b) Hill, J. A.; Thompson, A. L.; Goodwin, A. L. Dicyanometallates as model extended frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 5886−5896. (c) Schneider, L.; Sivchik, V.; Chung, K.-Y.; Chen, Y.-T.; Karttunen, A. J.; Chou, P. T.; Koshevoy, I. O. Cyclometalated platinum(II) cyanometallates: luminescent blocks for coordination self-assembly. *Inorg. Chem.* **2017**, *56*, 4459−4467.

(3) (a) Ohba, M.; Ōkawa, H. Synthesis and magnetism of multi-dimensional cyanide-bridged bimetallic assemblies. *Coord. Chem. Rev.* **2000**, *198*, 313−328. (b) Allen, G. C.; Hush, N. S. Prog. Intervalence-transfer absorption. Part 1. Qualitative evidence for intervalence-transfer absorption in inorganic systems in solution and in the solid state. *Inorg. Chem.* **2007**, *8*, 357−389. (c) Buser, H. J.; Ludi, A.; Petter, W.; Schwarzenbach, D. Single-crystal study of Prussian blue: $Fe_4[Fe(CN)_6]_2{\cdot}14H_2O$. *J. Chem. Soc., Chem. Commun.* **1972**, 1299. (d) Shores, M. P.; Beauvais, L. G.; Long, J. R. Cluster-expanded Prussian blue analogues. *J. Am. Chem. Soc.* **1999**, *121*, 775−779. (e) Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R. Expanded Prussian blue analogues incorporation $[Re_6Se_8(CN)_6]^{3-/4-}$ clusters: adjusting porosity via charge balance. *J. Am. Chem. Soc.* **2001**, *123*, 8022−8032. (f) Liu, Q.; Zhang, W.-H.; Lang, J.-P. Versatile thiomolybdate(thiotungstate)-copper-sulfide clusters and multidimensional polymers linked by cyanides. *Coord. Chem. Rev.* **2017**, *350*, 248−274.

(4) (a) Catala, L.; Gacoin, T.; Boilot, J. P.; Riviere, E.; Paulsen, C.; Lhotel, E.; Mallah, T. Cyanide-bridged Cr^{III}-Ni^{II} superparamagnetic nanoparticles. *Adv. Mater.* **2003**, *15*, 826−829. (b) Bonhommeau, S.; Molnár, G.; Galet, A.; Zwick, A.; Real, J. A.; McGarvey, J. J.; Bousseksou, A. One shot laser pulse induced reversible spin transition in the spin-crossover complex $[Fe(C_4H_4N_2)\{Pt(CN)_4\}]$ at room temperature. *Angew. Chem.* **2005**, *117*, 4137−4141. (c) Bonhommeau, S.; Molnár, G.; Galet, A.; Zwick, A.; Real, J. A.; McGarvey, J. J.; Bousseksou, A. One shot laser pulse induced reversible spin transition in the spin-crossover complex $[Fe(C_4H_4N_2)\{Pt(CN)_4\}]$ at room temperature. *Angew. Chem., Int. Ed.* **2005**, *44*, 4069−4073. (d) Wang, S.; Ding, X.-H.; Li, Y.-H.; Huang, W. Dicyanometalate chemistry: a type of versatile building block for the construction of cyanide-bridged molecular architectures. *Coord. Chem. Rev.* **2012**, *256*, 439−464.

(5) Williams, D.; Kouvetakis, J.; O'Keeffe, M. Synthesis of nanoporous cubic $In(CN)_3$ and $In_{1-X}Ga_X(CN)_3$ and corresponding inclusion compound. *Inorg. Chem.* **1998**, *37*, 4617−4620.

(6) (a) Brinzei, D.; Catala, L.; Mathonière, C.; Wernsdorfer, W.; Gloter, A.; Stephan, O.; Mallah, T. Photoinduced superparamagnetism in trimetallic coordination nanoparticles. *J. Am. Chem. Soc.* **2007**, *129*, 3778−3779. (b) Catala, L.; Brinzei, D.; Prado, Y.; Gloter, A.; Stephan, O.; Rogez, G.; Mallah, T. Core-multishell magnetic coordination nanoparticles: toward multifunctionality on the nanoscale. *Angew. Chem., Int. Ed.* **2009**, *48*, 183−187. (c) Prado, Y.; Lisnard, L.; Heurtaux, D.; Rogez, G.; Gloter, A.; Stéphan, O.; Dia, N.; Rivière, E.; Catala, L.; Mallah, T. Tailored coordination nanoparticles: assessing the magnetic single-domain critical size. *Chem. Commun.* **2011**, *47*, 1051−1053.

(7) (a) Thomsen, K. N.; Baldwin, R. P. Amperometric detection of non-electroactive cations in flow systems at a cupric hexacyanoferrate electrode. *Anal. Chem.* **1989**, *61*, 2594−2598. (b) Tani, Y.; Eun, H.; Umezawa, Y. A cation selective electrode based on copper (II) and nickel (II) hexacyanoferrates: dual response mechanisms, selective uptake or adsorption of analyte cations. *Electrochim. Acta* **1998**, *43*, 3431−3441. (c) Jiménez, J.-R.; Sugahara, A.; Okubo, M.; Yamada, A.; Chamoreau, L.-M.; Lisnard, L.; Lescouëzec, R. A $[Fe^{III}(Tp)(CN)_3]^-$ scorpionate-based complex as a building block for designing ion storage hosts (Tp: hydrotrispyrazolylborate). *Chem. Commun.* **2018**, *54*, 5189−5192.

(8) (a) Vogler, A.; Osman, A. H.; Kunkely, H. Heterobinuclear transition-metal complexes. Synthesis and optical metal to metal electron transfer. *Inorg. Chem.* **1987**, *26*, 2337−2340. (b) Bignozzi, C. A.; Indelli, M. T.; Scandola, F. Bis (2,2′B-bipyridine) ruthenium(II)-hexacyanochromate(III) chromophore-luminophore complexes. Intramolecular energy transfer, excited-state intervalence transfer, and doublet-doublet annihilation. *J. Am. Chem. Soc.* **1989**, *111*, 5192−5198. (c) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. Photoinduced electron and energy transfer in polynuclear complexes. *Top. Curr. Chem.* **1990**, *158*, 73−149. (d) Bignozzi, C. A.; Argazzi, R.; Chiorboli, C.; Roffia, S.; Scandola, F. Photoinduced intramolecular energy transfer processes in polynuclear ruthenium (II) polypyridine complexes. Design of long chain cyanobridged polynuclear species featuring vectorial energy transfer. *Coord. Chem. Rev.* **1991**, *111*, 261−266. (e) Scandola, F.; Argazzi, R.; Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi, M. A. Electronic coupling between remote metal centers in cyanobridged polynuclear complexes. *Coord. Chem. Rev.* **1993**, *125*, 283−292. (f) Cadranel, A.; Alborés, P.; Yamazaki, S.; Kleiman, V. D.; Baraldo, L. M. Efficient energy transfer via the cyanide bridge in dinuclear complexes containing Ru(II) polypyridine moieties. *Dalton Trans.* **2012**, *41*, 5343−5350.

(9) (a) Watzky, M. A.; Macatangay, A. V.; Van Camp, R. A.; Mazzetto, S. E.; Song, X. Q.; Endicott, J. F.; Buranda, T. Spectroscopic and electrochemical probes of electronic coupling in some cyanide-bridged transition metal donor/acceptor complexes. *J. Phys. Chem. A* **1997**, *101*, 8441−8459. (b) Wu, Y.; Pfennig, B. W.; Sharp, S. L.; Ludwig, D. R.; Warren, C. J.; Vicenzi, E. P.; Bocarsly, A. B. Light-induced multielectron charge transfer processes occurring in a series of group-8-platinum cyanobridged complexes. *Coord. Chem. Rev.* **1997**, *159*, 245−255. (c) Macatangay, A. V.; Endicott, J. F. Vibronic coupling in dicyano-complex-bridged mixed-valence complexes. Relaxation of vibronic constraints in systems with degenerate bridging-ligand and electron-transfer excited states. *Inorg. Chem.* **2000**, *39*, 437−446.

(10) (a) Matsui, K.; Nazeeruddin, Md. K.; Humphry-Baker, R.; Grätzel, M.; Kalyanasundaram, K. Transient absorption due to mixed valence species in the excited-state absorption spectra of cyano-bridged trinulear polypyridyl complexes of Ru(II). *J. Phys. Chem.* **1992**, *96*, 10587−10590. (b) Ponce, A.; Bachrach, M.; Farmer, P. J.; Winkler, J. R. Intramolecular electron transfer in cyanide-bridged ruthenium dimers. *Inorg. Chim. Acta* **1996**, *243*, 135−140.

(11) (a) Christensen, P. A.; Harriman, A.; Neta, P.; Richoux, M. C. Photo-oxidation of water using Prussian blue as catalyst. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2461−2466. (b) Tennakone, K.; Wickramanayake, S.; Fernando, N. Photocatalytic properties of cupric ferrocyanide. *Sol. Energy Mater.* **1987**, *16*, 467−470.

(12) Itaya, K.; Shoji, N.; Uchida, I. Catalysis of the reduction of molecular oxygen to water at Prussian blue modified electrodes. *J. Am. Chem. Soc.* **1984**, *106*, 3423−3429.

(13) (a) O'Regan, B.; Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature* **1991**, *353*, 737−740. (b) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. Design of antenna-sensitizer polynuclear complexes. Sensitization of titanium dioxide with $[Ru(bpy)_2(CN)_2]_2Ru(bpy(COO)_2)_2^{2-}$. *J. Am. Chem. Soc.* **1990**, *112*, 7099−7103. (c) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Meyer, G. J. Remote interfacial electron transfer from supramolecular sensitizers. *Inorg. Chem.* **1997**, *36*, 2−3.

(14) (a) Bignozzi, C. A.; Paradisi, C.; Roffia, S.; Scandola, F. Optical electron-transfer transitions in polynuclear complexes of the type $X(NH_3)_4RuNCRu(bpy)_2CNRu(NH_3)_4Y^{m+}$ (X = NH_3, py; Y = NH_3, py; m = 4−6). *Inorg. Chem.* **1988**, *27*, 408−414. (b) Bignozzi, C. A.; Roffia, S.; Chiorboli, C.; Davila, J.; Indelli, M. T.; Scandola, F. Oligomeric dicyano bis(polypyridine) ruthenium(II) complexes. Synthesis and spectroscopic and photophysical properties. *Inorg. Chem.* **1989**, *28*, 4350−4358. (c) Coe, B. J.; Meyer, T. J.; White, P. S. Cyano-bridged complexes of *trans*-Tetrakis(pyridine) ruthenium(II). *Inorg. Chem.* **1995**, *34*, 3600−3609. (d) Herrera, J.-M.; Ward, M. D.; Adams, H.; Pope, S. J. A.; Faulkner, S. Polynuclear cyanoruthenate chromophores based on hexaaza-triphenylene containing up to twelve

DOI: 10.1021/acs.inorgchem.9b00072

cyanides: photophysical and structural properties. *Chem. Commun.* **2006**, 1851−1853. (e) Herrera, J.-M.; Pope, S. J. A.; Meijer, A. J. H. M.; Easun, T. L.; Adams, H.; Alsindi, W. Z.; Sun, X.-Z.; George, M. W.; Faulkner, S.; Ward, M. D. Photophysical and structural properties of cyanoruthenate complexes of hexaazatriphenylene. *J. Am. Chem. Soc.* **2007**, *129*, 11491−11504. (f) Cadranel, A.; Oviedo, P. S.; Alborés, P.; Baraldo, L. M.; Guldi, D. M.; Hodak, J. H. Electronic energy transduction from $\{Ru(py)_4\}$ chromophores to Cr(III) luminophores. *Inorg. Chem.* **2018**, *57*, 3042−3053.

(15) (a) Kalyanasundaram, K.; Grätzel, M.; Nazeeruddin, M. K. Luminescence and intramolecular energy-transfer processes in isomeric cyano-bridged rhenium(I)-rhenium(I) and rhenium(I)-rhenium(II)-rhenium(I) polypyridiyl complexes. *Inorg. Chem.* **1992**, *31*, 5243−5253. (b) Bignozzi, C. A.; Argazzi, R.; Chiorboli, C.; Scandola, F.; Dyer, R. B.; Schoonover, J. R.; Meyer, T. J. Vibrational and electronic spectroscopy of electronically excited polychromophoric ruthenium(II) complexes. *Inorg. Chem.* **1994**, *33*, 1652−1659. (c) Pfennig, B. W.; Cohen, J. L.; Sosnowski, I.; Novotny, N. M.; Ho, D. M. Synthesis, characterization, and intervalence charge transfer properties of a series of rhenium(I)-iron(III) mixed-valence compounds. *Inorg. Chem.* **1999**, *38*, 606−612. (d) Thompson, D. W.; Schoonover, J. R.; Meyer, T. J.; Argazzi, R.; Bignozzi, C. A. Excited state electronic properties of the $[(phen)(OC)_3Re^{I}(NC)Ru^{II}(bpy)_2(CN)]PF_6$ and $[(phen)(OC)_3Re^{I}(NC)Ru^{II}(bpy)_2(CN)]PF_6$ linkage isomers. *J. Chem. Soc., Dalton Trans.* **1999**, 3729.

(16) Bignozzi, C. A.; Argazzi, R.; Garcia, C. G.; Scandola, F.; Schoonover, J. R.; Meyer, T. J. Long-range energy transfer in oligomeric metal complex assemblies. *J. Am. Chem. Soc.* **1992**, *114*, 8727−8729.

(17) Pieslinger, G. E.; Albores, P.; Slep, L. D.; Coe, B. J.; Timpson, C. J.; Baraldo, L. M. and Baraldo, L. M. Communication between remote moieties in linear Ru-Ru-Ru trimetallic cyanide-bridged complexes. *Inorg. Chem.* **2013**, *52*, 2906−2917.

(18) Lo, L. T.-L.; Lai, S.-W.; Yiu, S.-M.; Ko, C.-C. A new class of highly solvatochromic dicyano rhenate(I) diimine complexes−synthesis, photophysics and photocatalysis. *Chem. Commun.* **2013**, *49*, 2311−2313.

(19) Chu, W.-K.; Ko, C.-C.; Chan, K.-C.; Yiu, S.-M.; Wong, F.-L.; Lee, C.-S.; Roy, V. A. L. A simple design for strongly emissive sky-blue phosphorescent neutral rhenium complexes: synthesis, photophysics, and electroluminescent devices. *Chem. Mater.* **2014**, *26*, 2544−2550.

(20) Ko, C.-C.; Ng, C.-O.; Yiu, S.-M. Luminescent rhenium(I) phenanthroline complexes with a benzoxazole-2-ylidene ligand: synthesis, characterization, and photophysical study. *Organometallics* **2012**, *31*, 7074−7084.

(21) Subasi, E.; Uğur, F.; Şentürk, O. S. Photochemical reactions of $Re(CO)_3Br$ with $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; 2, dppe; 3, dppp). *Transition Met. Chem.* **2004**, *29*, 16−18.

(22) Schmidt, S. P.; Trogler, W. C.; Basolo, F.; Urbancic, M. A.; Shapley, J. R. Pentacarbonyl rhenium halides. *Inorg. Synth.* **2007**, *28*, 160−165.

(23) Dows, D. A.; Haim, A.; Wilmarth, W. K. J. Infra-red spectroscopic detection of bridging cyanide groups. *J. Inorg. Nucl. Chem.* **1961**, *21*, 33−37.

(24) (a) Shriver, D. F. Preparation and structures of metal cyanide-Lewis acid bridge compounds. *J. Am. Chem. Soc.* **1963**, *85*, 1405−1408. (b) Bignozzi, C. A.; Scandola, F. Cyano-bridged ruthenium(II)/platinum(II) complexes: synthesis, photophysical properties, and excited-state redox behavior. *Inorg. Chem.* **1984**, *23*, 1540−1545.

(25) (a) Pombeiro, A. J. L.; Carvalho, M. F. N. N.; Hitchcock, P. B.; Richards, R. L. Preparation of the isocyanide complexes *trans*-$[ReCl(CNR)(dppe)_2]$ (R = Me or Bu^t) and their reactions with acid to give carbine complexes. X-ray crystal structure of *trans*-$[ReCl(CNHMe)(dppe)_2][BF_4]$. *J. Chem. Soc., Dalton Trans.* **1981**, 1629−1934. (b) Cheung, A. W.-Y.; Lo, L. T.-L.; Ko, C.-C.; Yiu, S.-M. Synthesis, functionalization, characterization, and photophysical study of carbonyl-containing isocyano rhenium(I) diimine complexes. *Inorg. Chem.* **2011**, *50*, 4798−4810. (c) Ko, C. C.; Siu, J. W.-K.; Cheung, A. W.-Y.; Yiu, S.-M. Synthesis, characterization, and photophysical and emission solvatochromic study of rhenium(I) tetra(isocyano) diimine complexes. *Organometallics* **2011**, *30*, 2701−2711.

(26) (a) Kalyanasundaram, K. Luminescence and redox reactions of the metal-to-ligand charge-transfer excited state of tricarbonylchloro-(polypyridyl) rhenium(I) complexes. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401−2415. (b) Worl, L. A.; Duesing, R.; Chen, P.; Ciana, L. D.; Meyer, T. J. Photophysical properties of polypyridyl carbonyl complexes of rhenium(I). *J. Chem. Soc., Dalton Trans.* **1991**, 849−858. (c) Kirgan, R. A.; Sullivan, B. P.; Rillema, D. P. Photochemistry and photophysics of coordination compounds: rhenium. *Top. Curr. Chem.* **2007**, *281*, 45−100. (d) Kumar, A.; Sun, S.-S.; Lees, A. J. Photophysics and photochemistry of organometallic rhenium diimine complexes. *Top. Organomet. Chem.* **2009**, *29*, 37−71. (e) Ko, C.-C.; Cheung, A. W.-Y.; Lo, L. T.-L.; Siu, J. W.-K.; Ng, C.-O.; Yiu, S.-M. Synthesis and photophysical study of new classes of luminescent isocyano rhenium(I) diimine complexes. *Coord. Chem. Rev.* **2012**, *256*, 1546−1555.

(27) Ko, C.-C.; Lo, L. T.-L.; Ng, C.-O.; Yiu, S.-M. Photochemical synthesis of intensely luminescent isocyano rhenium(I) complexes with readily tunable structural features. *Chem. - Eur. J.* **2010**, *16*, 13773−13782.

(28) Chakraborty, I.; Jimenez, J.; Sameera, W. M. C.; Kato, M.; Mascharak, P. K. Luminescent Re(I) carbonyl complexes as trackable photoCORMs for CO delivery to cellular targets. *Inorg. Chem.* **2017**, *56*, 2863−2873.

(29) (a) Lees, A. J. Luminescence properties of organometallic complexes. *Chem. Rev.* **1987**, *87*, 711−743. (b) Stufkens, D. J. The remarkable properties of α-diimine rhenium tricarbonyl complexes in their metal-to-ligand charge-transfer (MLCT) excited states. *Comments Inorg. Chem.* **1992**, *13*, 359−385. (c) Striplin, D. R.; Crosby, G. A. Photophysical investigations of rhenium(I)Cl-$(CO)_3$(phenanthroline) complexes. *Coord. Chem. Rev.* **2001**, *211*, 163−175.

(30) (a) Luong, J. C.; Nadjo, L.; Wrighton, M. S. Ground and excited state electron transfer processes involving *fac*-tricarbonylchloro(1,10-phenanthroline)rhenium(I). Electrogenerated chemiluminescence and electron transfer quenching of the lowest excited state. *J. Am. Chem. Soc.* **1978**, *100*, 5790−5795. (b) Ng, C.-O.; Lo, L. T.-L.; Ng, S.-M.; Ko, C.-C.; Zhu, N. A new class of isocyanide-containing rhenium(I) bipyridyl luminophore with readily tunable and highly environmentally sensitive excited-state properties. *Inorg. Chem.* **2008**, *47*, 7447−7449.

(31) Ko, C.-C.; Kwok, W.-M.; Yam, V. W.-W.; Phillips, D.-L. Triplet MLCT photosensitization of the ring-closing reaction of diarylethenes by design and synthesis of a photochromic rhenium(I) complex of a diaryethene-containing 1,10-phenanthroline ligand. *Chem. - Eur. J.* **2006**, *12*, 5840−5848.

(32) Tsubaki, H.; Tohyama, S.; Koike, K.; Saitoh, H.; Ishitani, O. Effect of intramolecular $\pi-\pi$ and CH$-\pi$ interactions between ligands on structure, electrochemical and spectroscopic properties of *fac*-$[Re(bpy)(CO)_3(PR_3)]^+$ (bpy = 2,2′-bipyridine; PR_3 = trialkyl or triarylphosphines). *Dalton Trans.* **2005**, 385−395.