Systematic Synthesis, Isolation, and Photophysical Properties of Linear-shaped Re(I) Oligomers and Polymers with 2 – 20 units.

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Supporting Information

Figure S1. ESI MS spectra of a CH_2Cl_2 solution containing $[\text{Re2ac}]^{2+}(\text{CF}_3\text{SO}_3^-)_2$ before and after irradiation. The eluent was MeCN.

Figure S2. ESI MS spectra of a CH_2Cl_2 solution containing $[\text{Re4ac}]^{4+}(\text{CF}_3\text{SO}_3^-)_4$ before and after irradiation. The eluent was MeCN.

Figure S3. Chromatograms of analytical SEC. Reaction mixture (a), with isolation of $[\text{Re5ac}]^{5+}$, $[\text{Re10ac}]^{10+}$, $[\text{Re15ac}]^{15+}$, and $[\text{Re20ac}]^{20+}$. The eluent was a 1:1 (v/v) mixture of methanol and acetonitrile containing 0.3 M $\text{CH}_3\text{CO}_2\text{NH}_4$, and the flow rate was 5.0 ml min^{-1} . The detection wavelength was 360 nm.

Figure S4. Packing diagram of $[\text{Re2ac}]^{2+}(\text{PF}_6^-)_2$, PF_6^- and hydrogen atoms omitted for clarity.

Figure S5. Emission decay curve of $[\text{Re8ac}]^{8+}$ obtained with excitation wavelength of 400 nm, and monitor wavelength of 600 nm.

Table S1. Crystallographic Data for PF₆[−] salts of [Re2ac]²⁺, [Re3ac]³⁺, [Re3et]³⁺, and [Re4et]⁴⁺

complex	[Re2ac] ²⁺ (PF ₆ [−]) ₂	[Re3ac] ³⁺ (PF ₆ [−]) ₃
empirical formula	C ₅₂ H ₃₆ F ₁₂ N ₄ O ₆ P ₄ Re	C ₉₃ H _{68.5} F ₁₈ N _{7.5} O ₈ P ₇ Re
formula weight	2	3
crystal system	triclinic	tetragonal
space group	<i>P</i> -1	<i>I</i> 4/m
<i>a</i> /Å	11.927(3)	24.9802(1)
<i>b</i> /Å	12.952(3)	24.9802(1)
<i>c</i> /Å	9.752(2)	30.8551(2)
α /deg	94.00(2)	90
β /deg	94.03(2)	90
γ /deg	103.22(2)	90
<i>V</i> /Å ³	1457.1	19253.9
<i>Z</i>	1	8
<i>T</i> /K	298	123
<i>R</i> _{int}	0.012	0.0649
number of total reflections	7833	13226
number of parameters	379	672
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0519	0.0388
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.0913	0.1123
GOF ^c on <i>F</i> ²	1.001	1.02

Table S1. (Continued)

complex	[Re3et] ³⁺ (PF ₆ ⁻) ₃	[Re4et] ⁴⁺ (PF ₆ ⁻) ₄
empirical formula	C ₉₉ H ₉₀ F ₁₈ N ₆ O ₁₁ P ₇ Re	C ₁₂₈ H ₁₀₄ F ₂₄ N ₈ O ₁₀ P ₁₀ Re
formula weight	2657.2	3424.8
crystal system	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	14.4854(2)	15.8437(7)
<i>b</i> /Å	16.5421(2)	16.8427(5)
<i>c</i> /Å	22.1601(4)	25.4088(10)
α /deg	86.8517(8)	78.1431(14)
β /deg	79.2971(8)	85.046(2)
γ /deg	82.7139(13)	83.545(5)
<i>V</i> /Å ³	5172.8	6579.7
<i>Z</i>	2	2
<i>T</i> /K	223	123
<i>R</i> _{int}	0.0506	0.0463
number of total reflections	27558	24255
number of parameters	1334	1657
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0418	0.0519
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.0939	0.1459
GOF ^c on <i>F</i> ²	0.881	0.925

^a $R_1 = \sum(|F_O| - |F_C|) / \sum|F_O|$. ^b $wR_2 = [\sum[w(F_O^2 - F_C^2)^2] / \sum[w(F_O^2)^2]]^{1/2}$. ^c $GOF = [\sum w(|F_O|^2 - |F_C|^2)^2 / (m - n)]^{1/2}$, where *m* = number of reflections and *n* = number of parameters.