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Supplementary Information

Chiral Phosphorescent Probes for Amino Acids: Hybrids of Iridium(III) Complexes with Synthetic Saponite

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Contnets

S1· ^{1}H NMR and mass spectra

S2. Chromatogram for diastereomeric separation

S3. Quenching of Ir-1 and Ir-2 by *RS*-tryptophan methyl ester in methanol

S4. The dynamic Stern-Volmer plots for quenching of Ir-1 in a synthetic saponite suspension

S5. Quenching effects of amino acid methyl esters

S6. Enantiomeric effects of quenching for pairs of *R*- or *S*-tryptophan methyl ester and Δ- or Λ-Ir-1.

S7. Chromatogram for optical resolution and CD spectra of DNB-al-Me

S8. The transient measurements of the emission from Ir-1 in the presence of *R*- or *S*-DNB-al-Me.

S9. The calculation of quantum yield of emission

S1. ^{1}H NMR and mass spectra

R-pep-bpy = 4,4’-bis((*R*-1,2-dimethylpropyl)aminocarbonyl-2,2’-bipyridine)

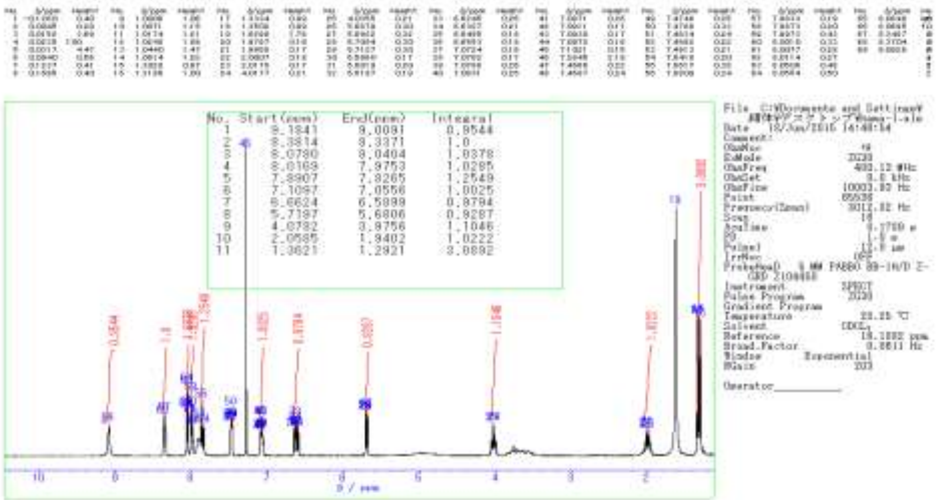
^{1}H NMR (chloroform-*d*, 400MHz, 25 °C): δ 8.85 (d, *J* = 5.0 Hz, 2H), 8.65 (s, 2H), 7.83 (t, *J* = 5.0 Hz, 2H), 6.21 (d, *J* = 8.4 Hz, 2H), 4.15 (dd, *J* = 8.7, 6.6 Hz, 2H), 1.89 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 6H), 1.02 (dd, *J* = 6.8, 4.8 Hz, 12H).

[Ir(dfppy)$_2$(*R*-pep-bpy)]$^+$ (Ir-1)

^{1}H NMR (acetornitrile-*d$_3$*, 400MHz, 25 °C): δ 8.96 (s, 2H), 8.32 (d, *J* = 5.5 Hz, 2H), 7.90 (t, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.60 (d, *J* = 5.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 6.72 (m, 2H), 5.71(dd, *J* = 8.0, 2.4 Hz, 2H), 3.95(m, 2H), 1.84 (m, 2H), 1.19 (d, *J* = 6.9 Hz, 6H), 0.94 (dd, J = 6.4, 2.2 Hz, 12H); MS (m/z; ESI$^+$): [M]$^+$ 955.2935 (calculated for [Ir(dfppy)$_2$(C$_1$-bpy)]$^+$; $C_{44}H_{42}F_4IrN_6O_2$), 955.2917 (experimentally obtained).

[Ir(piq)$_2$(*R*-pep-bpy)]$^+$ (Ir-2)

^{1}H NMR (acetornitrile-*d$_3$*, 400 MHz, 25 °C): δ 9.01 (dd, *J* = 6.5, 3.4Hz, 2H), 8.96 (s, 2H), 8.39 (d, *J* = 8.00 Hz, 2H), 7.95 (d, *J* = 5.6 Hz, 2H), 7.83 (t, *J* = 3.2 Hz, 4H), 7.75 (dd, *J* = 5.6, 1.3 Hz, 2H), 7.48 (dd, *J* = 6.5, 1.8 Hz, 2H), 7.41 (d, *J* = 6.5 Hz, 4H), 7.27 (d, *J* = 6.9 Hz, 4H), 7.14 (m, 2H), 6.89 (m, 2H), 6.30 (dd, *J* = 7.5, 1.2 Hz, 2H), 3.90 (m, 2H), 1.82 (m, 2H), 1.17 (d, *J* = 6.9 Hz, 6H), 0.93 (dd, J = 6.7, 2.2 Hz, 12H); MS (m/z; ESI$^+$): [M]$^+$ 983.3624 (calculated for [Ir(piq)$_2$(C$_1$-bpy)]$^+$; $C_{50}H_{52}IrN_6O_2$) 983.3601 (experimentally obtained).



No.	Start(ppm)	End(ppm)	Integral
1	9.1841	9.0081	0.9544
2	8.3814	8.3371	1.0
3	8.0780	8.0404	1.0378
4	8.0169	7.9753	1.0285
5	7.8907	7.8265	1.2549
6	7.1097	7.0556	1.0025
7	6.6624	6.5899	0.8794
8	5.7197	5.6806	0.9287
9	4.0782	3.8756	1.1046
10	2.0585	1.9402	1.0222
11	1.3621	1.2921	3.0892

Fig. S1 The full chart of ^{1}H NMR spectrum of [Ir(dfppy)$_2$(C$_{12}$-bpy)]ClO$_4$ in CDCl$_3$

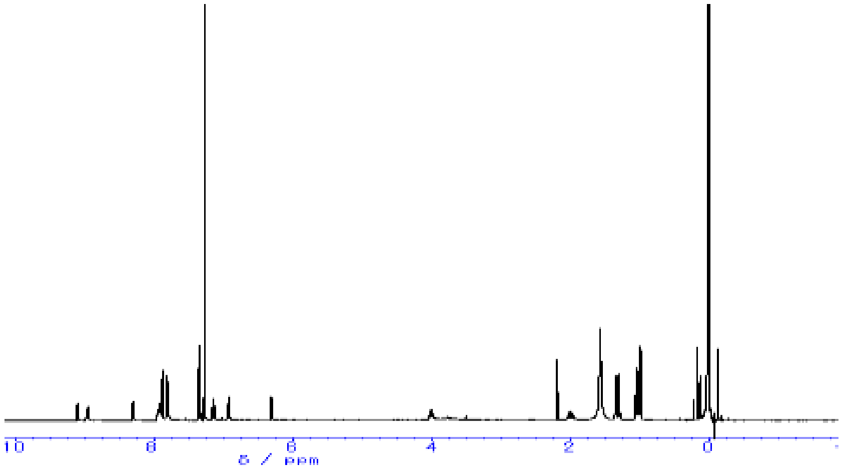


Fig. S2. The full chart of ^{1}H NMR spectrum of [Ir(piq)$_2$(C$_{12}$-bpy)]ClO$_4$ in CDCl$_3$

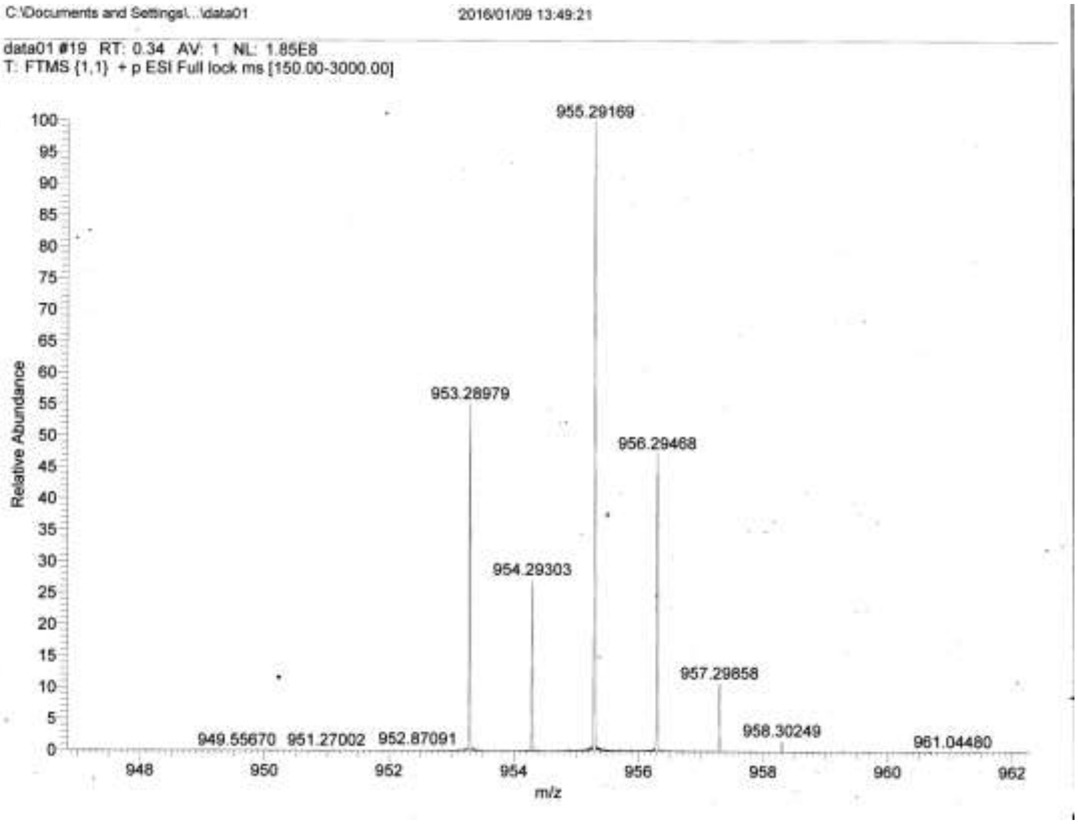


Fig.S3. The full chat of mass spectrum of [Ir(dfppy)$_2$(*R*-pep-bpy)]$^+$ (Ir-1)

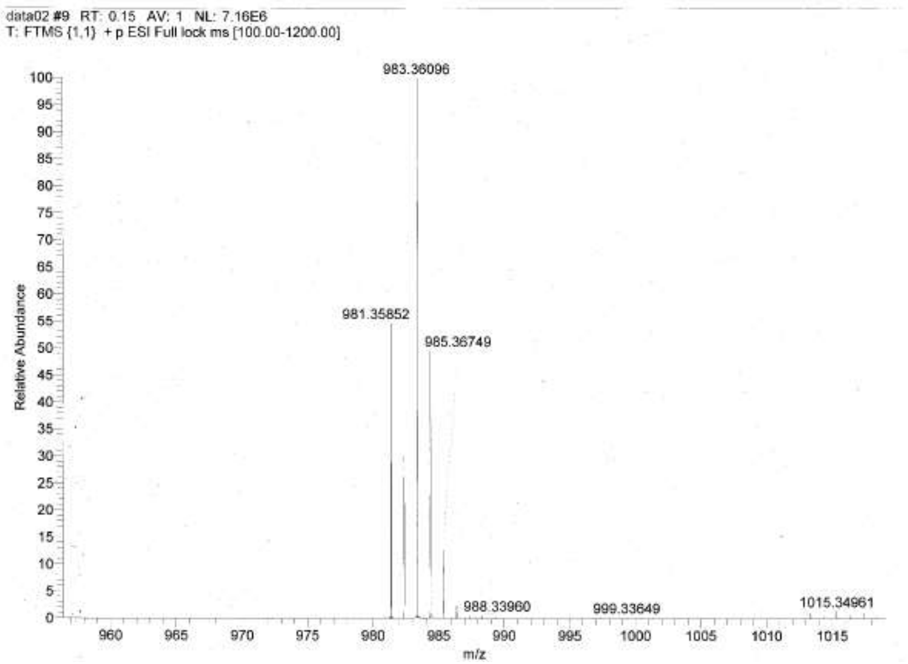


Fig. S4. The full chart of mass spectrum of [Ir(piq)$_2$(*R*-pep-bpy)]$^+$ (Ir-2)

S2. Chromatogram for diastereomeric separation

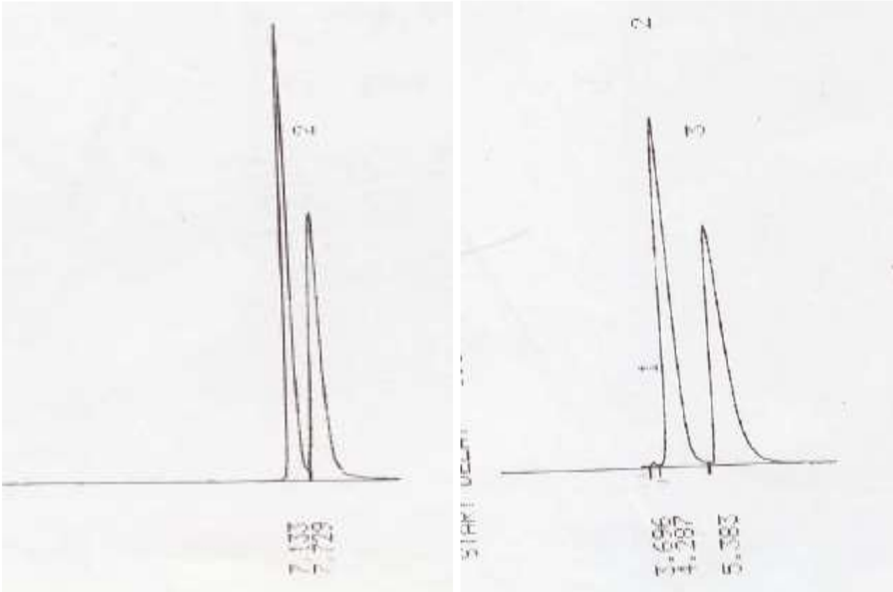


Figure S5. Chromatogram for resolving iridium(III) complexes: (left) **Ir-1** and (right) **Ir-2**.

The flow rate was 0.5 mLmin^{-1} and the monitoring wavelength 400 nm. The used column was a CHIRALPACK IA (Daicel, Japan). An eluting solvent was $CH_3CN/CF_3COOH/NH(CH_2CH_3)_2$ = 100/0.1/0.1.

S3. Quenching of Ir-1 and Ir-2 by *RS*-tryptophan methyl ester in methanol

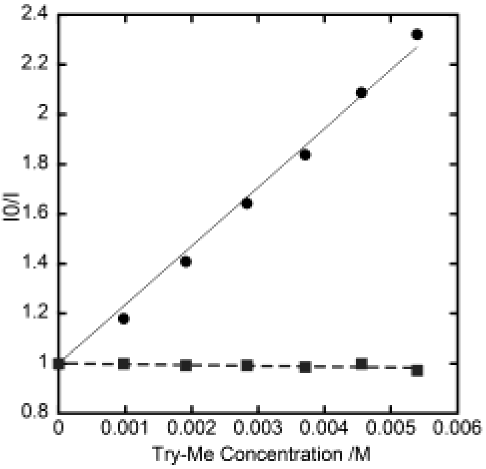


Figure S6. The Stern-Volmer plots for the quenching of **Ir-1** (filled circle) and **Ir-2** (filled square) by *RS*-tryptophan methyl ester in methanol. The emission was monitored at 570 nm (**Ir-1**) or 650 nm (**Ir-2**), when the iridium(III) complexes were irradiated at 350 nm: [**Ir-1**] = 9.1×10^{-5}M and [**Ir-2**] = 6.6×10^{-5}M. The Stern-Volmer constant (K_{SV}) was obtained to be 235 ± 5 M^{-1} for **Ir-1** and 0 ± 5 M^{-1} for **Ir-2**, respectively.

S4. The dynamic Stern-Volmer plots for quenching of Ir-1 in a synthetic saponite suspension

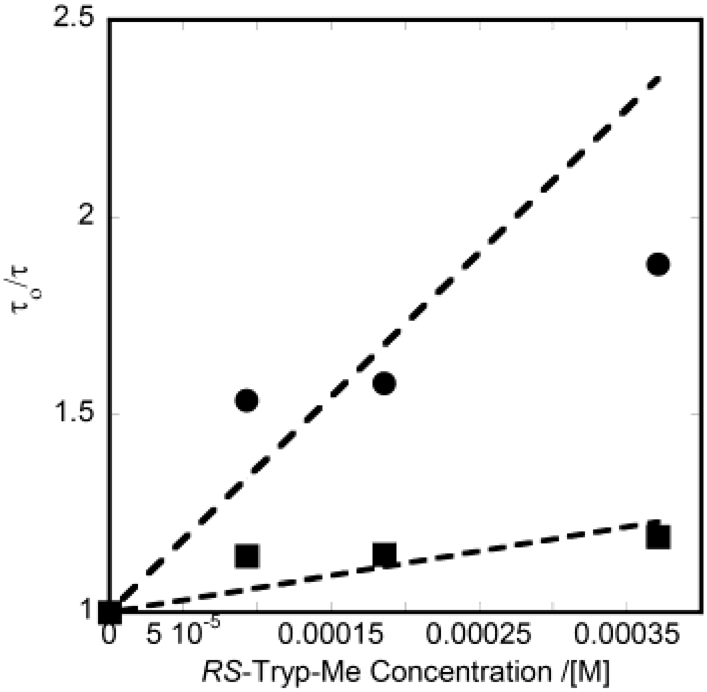
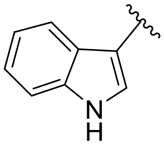
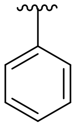
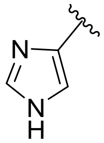
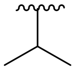


Figure S7. The dynamic Stern-Volmer Plots for the quenching of **Ir-1** by tryptophan methyl ester in an aqueous suspension of synthetic saponite according to equation (3) in the text. Solid circles and triangles denote the fast and slow relaxations, respectively. The experimental conditions were the same as in Figure 5 in the text. No accurate lifetime was determined at [*RS*-tryp-Me] higher than 4×10^{-4} M due to the instrumental limitation. The results are summarized in Table 2 in the text.

S5. Quenching effects of amino acid methyl esters

The following table summarizes the average values of K_{sv} (K_{svav}) for various amino acid methyl esters when the emission from **Ir-1** was measured.

Table S1. Average Stern-Volmer constants or various amino acid methyl esters when the emission from **Ir-1**

Amino acid methyl ester	Tryptophan methyl ester	Alanine methyl ester	Phenyl-alanine methyl ester	Histidine methyl ester	Valine methyl ester
Residue structure		CH_3			
K_{svav} (M^{-1}) for **Ir-1**	8400	16.0	213	-80.9*	75.6

（ * Emission increased on adding an amino acid methyl ester.）

S6. Enantiomeric effects of quenching for pairs of *R*- or *S*-tryptophan methyl ester and Δ- or Λ-Ir-1.

The following table shows the average Stern-Volmer constants for four pairs of chiral tryptophan methyl ester and **Ir-1**. A solvent was 3:1(v/v) water/methanol. The emission was measured at λ_{em} = 579 nm under the excitation at λ_{ex} = 350 nm. The concentrations were [**Ir-1**] = 3.0×10^{-6} M and [SAP] = 4.4×10^{-4} M in terms of cation-exchange capacity.

Table S2. Average Stern-Volmer constants for four pairs of chiral tryptophan methyl ester and **Ir-1**

Emitter	**Quencher**	Slope(M^{-1}) (slopes of Stern-Volmer plots)
Λ-*R* - Ir-1	*S*-tryptophan methyl ester	8011
Λ-*R* - Ir-1	*R*-tryptophan methyl ester	8019
Δ-*R* - Ir-1	*S*-tryptophan methyl ester	9161
Δ-*R* - Ir-1	*R*-tryptophan methyl ester	7897

S7. Chromatogram for optical resolution and CD spectra of DNB-al-Me

Figure S8. The chromatogram for resolving a racemic mixture of DNB-al-Me. A flow rate was 1.0 mLmin^{-1} and the monitoring wavelength 260 nm. The used column was a RU-1 Ceramosphere (Shiseido Inc., Japan). An eluting solvent was methanol. The first and second peaks corresponded to *R*- and *S*-DNB-al-Me, respectively.

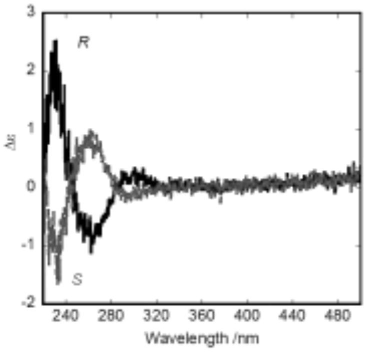


Figure S9. The CD spectra of resolved *R*- and *S*-DNB-al-Me enantiomers. A solvent was methanol.

S8. The transient measurements of the emission from Ir-1 in the presence of *R*- or *S*-DNB-al-Me.

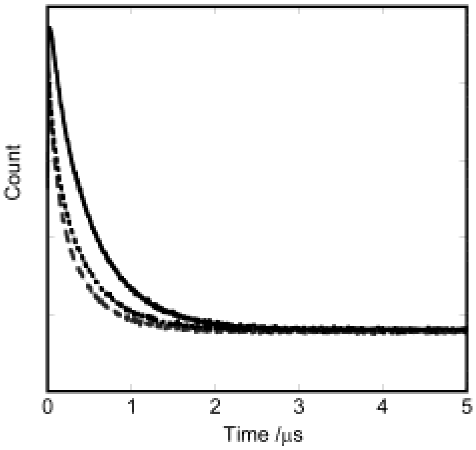


Figure S10. The decay of the emission from **Ir-1** to see the effects of enantiomeric DNB-al-Me. The emission was measured on irradiating SAP suspensions at 355 nm: (1) SAP/Λ-**Ir-1** only (bald solid); (2) SAP/Λ-**Ir-1**/*S*-DNB-al-Me (broken) and (3) SAP/Λ-**Ir-1**/*R*-DNB-al-Me (dotted). The medium was 3:1 (v/v) water/methanol. The concentration of SAP was 2.5×10^{-4} eq L^{-1} CEC and [Ir-1] = 2.0×10^{-6} M. The added concentration of *S*- or *R*-DNB-al-Me was 2.0×10^{-4} M.

The above curves were analyzed in terms of two exponential decay processes. The following table summairzes the results: τ_1 (fast life time), τ_2 (slow life time), f_1 (the fraction of the fast component) and f_2 (the fraction of the slow component).

Table S3. Summary of lifetimes

	(1) SAP/Λ-**Ir-1**	(2) SAP/Λ-**Ir-1**/*S*-DNB-al-Me	(3) SAP/Λ-**Ir-1**/*R*-DNB-al-Me
τ_1 (μs)	0.43	0.18	0.27
τ_2 (μs)	0.81	0.45	0.57
f1	0.81	0.33	0.56
f2	0.19	0.67	0.44

S9. The calculation of quantum yield of emission

The quantum yield of emission was analyzed according to the following equation:

$$\Phi = \Phi_{st}(\frac{A_{st}}{A})(\frac{D}{D_{st}})(\frac{n^2}{n_{st}^2})$$

where Φ is quantum yield for an iridium(III) complex, *A* absorbance at 430 nm, *D* an irradiated area, *n* refractive index. The subscript *st* means the standard value for $[Ru(bpy)_3]^{2+}$ (Φ_{st} = 0.028). The wavelength of excitation (λ_{ex}) was 430 nm (ref. K. Nakamaru, K., *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697-2705). .

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