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Acid-base-induced *fac* → *mer* isomerization of luminescent iridium(III) complexes†

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Luminescent Ir(C[^]N)₃ complexes (C[^]N = cyclometalated arylpyridine ligand) exist in the form of two stable isomers with distinct photophysical and electrochemical properties: *fac* and *mer*. Herein, we show that *fac*-Ir(C[^]N)₃ complexes can be converted into the thermodynamically less stable *mer* forms by a consecutive reaction with first acid and then base. The chemically induced isomerization is fast, quantitative, and stereoselective, and it can be inverted by light. The new isomerization process opens the possibility to use highly luminescent Ir(C[^]N)₃ complexes as molecular switches.

Introduction

Iridium(III) complexes with cyclometalated arylpyridine ligands (C[^]N ligands) display intriguing photophysical and chemical properties. Noteworthy characteristics include high photoluminescence quantum yields, reversible redox transitions, a pronounced chemical and thermal stability, and the possibility to tune the emission color, the phosphorescence lifetime, and the redox properties by structural modifications.¹ The unique properties of Ir(C[^]N)₃ complexes have led to diverse applications.^{1–10} For example, Ir(C[^]N)₃ complexes have been used as emitters in organic light-emitting diodes (OLEDs),^{2,3} as photoredox catalysts,^{4,5} as chemical or biological probes,^{6–8} and as building blocks for supramolecular assemblies.^{9,10}

Ir(C[^]N)₃ complexes form two stable isomers with distinct photophysical and electrochemical properties: *fac* and *mer*.¹¹ The *mer* isomers are thermodynamically less stable than the *fac* isomers. By adjusting the reaction conditions, it is possible to obtain the *mer* isomer in a kinetically controlled reaction.^{11,12} A *mer* → *fac* isomerization can be achieved at high temperature or by irradiation.^{11,13–15} The inverse *fac* → *mer* isomerization, which is thermodynamically uphill, has not been reported so far.

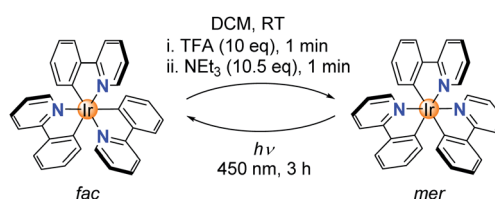
Herein, we show that a *fac* → *mer* isomerization can be achieved by a consecutive reaction with first acid and then base. The chemically induced isomerization allows using highly luminescent Ir(C[^]N)₃ complexes as molecular switches.

Results and discussion

While studying the chemistry of *fac*-Ir(ppy)₃ (ppy = metalated 2-phenylpyridine), we made a surprising observation: when a solution of *fac*-Ir(ppy)₃ in dichloromethane was treated in a successive fashion with first trifluoroacetic acid (TFA, 10 equiv.) and then with triethylamine (10.5 equiv.), a quantitative conversion into the *mer* isomer was observed (Scheme 1).

The chemically induced transformation of *fac*-Ir(ppy)₃ into *mer*-Ir(ppy)₃ was followed by ¹H NMR spectroscopy using CD₂Cl₂ as solvent. The TFA treatment resulted in the rapid (<1 min) formation of a defined complex of low symmetry, with three sets of signals for the three ligands (Fig. 1a). Furthermore, the NMR data indicated that protonation had occurred at one of the phenyl groups, thereby converting a chelating, anionic C[^]N ligand into a monodentate, neutral N-donor ligand.

Attempts to characterize the TFA adduct by single crystal X-ray crystallography were not successful. However, when using bistriflimidic acid (HNTf₂) instead of TFA, we were able to crystallize the 'open form'. The result of a crystallographic analysis is depicted in Fig. 1b. In line with the NMR data, the cationic Ir complex features two orthometalated 2-phenylpyridine ligands and one neutral 2-phenylpyridine ligand, which is bound *via* the pyridine group to the metal. One C–H group of the phenyl ring forms an agostic interaction¹⁶ with the cationic Ir center (Ir...H ~ 1.97 Å; Ir–H–C ~ 115°). When the



Scheme 1 Interconversion of *fac*-Ir(ppy)₃ and *mer*-Ir(ppy)₃.

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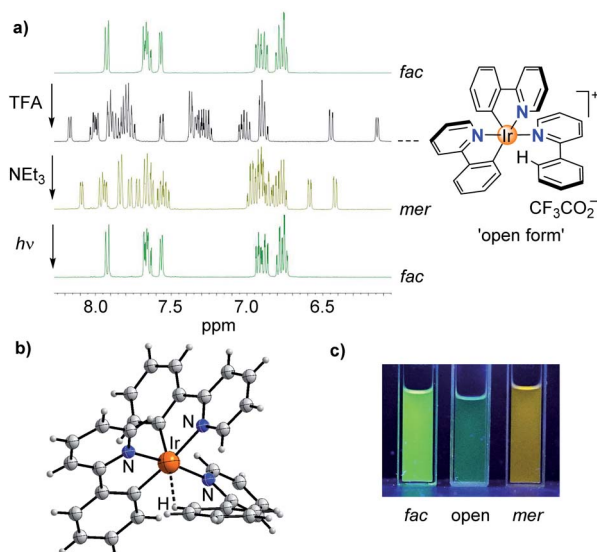


Fig. 1 (a) ¹H NMR spectra (400 MHz, CD₂Cl₂, aromatic region) for the conversion of *fac*-Ir(ppy)₃ into *mer*-Ir(ppy)₃ and back. (b) Molecular structure of [Ir(ppy)₂(Hppy)](NTf₂) in the crystal with thermal ellipsoids at 50% probability; the anion is not shown for clarity. (c) Photos of solutions containing *fac*-Ir(ppy)₃, [Ir(ppy)₂(Hppy)](O₂CCF₃) ('open form'), and *mer*-Ir(ppy)₃ under UV-light (λ_{ex} = 366 nm).

agostic interaction is taken into account, the coordination environment around Ir can be described as distorted octahedral. The open form has a meridional arrangement of the three N-donor atoms, and a base-induced metalation is primed to give the *mer* isomer of Ir(ppy)₃, as found experimentally. Within one minute after the addition of NEt₃, a quantitative formation of *mer*-Ir(ppy)₃ was observed (Fig. 1a). As described in the literature,^{11–15} it is possible to convert the *mer* isomer back into the *fac* isomer by irradiation. For this purpose, we have used a 90 W LED lamp with an emission maximum at 450 nm. A clean back-isomerization was achieved within 3 h, as evidenced again by ¹H NMR spectroscopy (Fig. 1a). The *fac* and the *mer* isomer of Ir(ppy)₃ show distinct emission colours and intensities, with a weaker, red-shifted emission for the *mer* form (Fig. 1c).¹¹ The open form [Ir(ppy)₂(Hppy)](O₂CCF₃) is largely non-luminescent.

The acid-base reaction accompanying the transformation of *fac*-Ir(ppy)₃ to *mer*-Ir(ppy)₃ results in the formation of (HNET₃)(O₂CCF₃) (Fig. 2a). In order to examine if the presence of this salt would compromise subsequent isomerization steps, we

have performed multiple *fac* → *mer* → *fac* cycles in the same reaction flask without separation/purification steps. The conversion efficiency was monitored by recording the emission spectra after each isomerization. The results indicate that for ten cycles, neither the chemically induced *fac* → *mer* isomerization nor the photochemical *mer* → *fac* isomerization is compromised to a significant extent by the presence of accumulating amounts of salt (ESI, Fig. S37†). The robustness of the switching process was substantiated by ¹H NMR studies in CD₂Cl₂. After three *fac* → *mer* → *fac* cycles, only small amounts of side products could be detected by ¹H NMR spectroscopy (ESI, Fig. S2–4†).

Next, we examined if other Ir(C[^]N)₃ complexes would also undergo acid-base-induced *fac* → *mer* isomerizations. Complexes with orthometalated *p*-tolylpyridine (tpy), 2-(4-methoxyphenyl)pyridine (meppy) and 2-(4-*tert*-butylphenyl)pyridine (buppy) ligands behaved in a similar fashion as Ir(ppy)₃: a clean and fast *fac* → *mer* conversion could be induced by consecutive addition of TFA (5–10 equiv.) and NEt₃ (5.5–10.5 equiv.) (Scheme 2). A quantitative back-isomerization was achieved by irradiation with blue light (ESI, Fig. S5–10, S17†). For complexes based on 2-(4-fluorophenyl)pyridine (Hfppy) and 2-(2,4-difluorophenyl)pyridine (Hdfppy), on the other hand, TFA addition did not result in the formation of an open form. We hypothesized that the reduced basicity of the fluorinated phenyl group was responsible for the lack of reactivity. Indeed, the *fac* → *mer* isomerization of *fac*-Ir(fppy)₃ and *fac*-Ir(dfppy)₃ was achieved with the stronger acid HNTf₂ (2 and 5 equiv., respectively) (Fig. S11–16 and S18†).

The protonated complexes [Ir(C[^]N)₂(HC[^]N)]⁺ feature a monodentate N-donor ligand. This ligand is expected to be more labile than the chelating C[^]N ligands. It was therefore conceivable that ligand exchange processes can occur during isomerization at the stage of the 'open form'. In order to evaluate if ligand scrambling can happen, we have examined the *fac* → *mer* → *fac* isomerization of an equimolar mixture of *fac*-Ir(ppy)₃ and *fac*-Ir(tpy)₃ in CD₂Cl₂. Analysis of the mixture after TFA/NEt₃ treatment by ¹H NMR spectroscopy showed the clean formation of the homoleptic complexes *mer*-Ir(ppy)₃ and *mer*-Ir(tpy)₃ (Scheme 3 and ESI, Fig. S39†). The results of the NMR analysis were corroborated by high-resolution mass spectrometry: signals of the heteroleptic complexes *mer*-Ir(ppy)₂(tpy) and

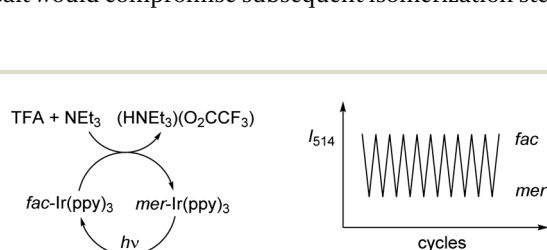
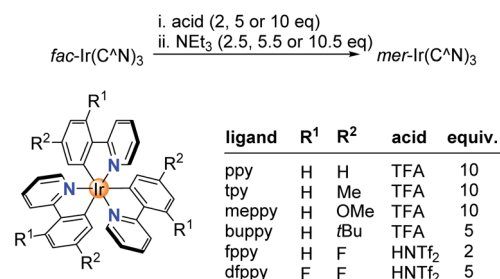
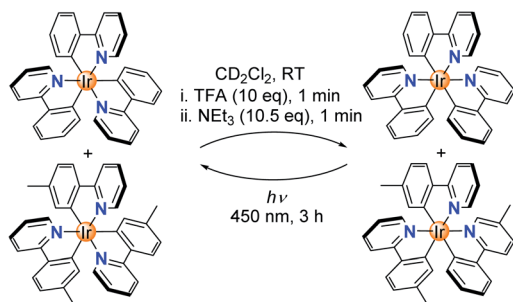


Fig. 2 Acid-base treatment followed by irradiation allows repetitive cycling between *fac*- and *mer*-Ir(ppy)₃. The interference of accumulating (HNET₃)(O₂CCF₃) is low for the first ten cycles, as evidenced by spectroscopic monitoring.



Scheme 2 Chemically induced *fac* → *mer* isomerizations are possible for different Ir(C[^]N)₃ complexes using either TFA or HNTf₂ for the protonation step.

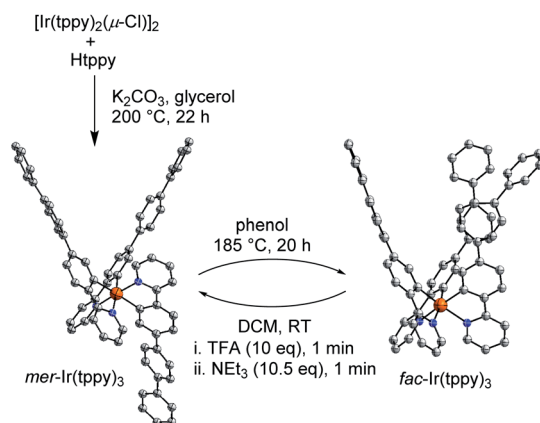


Scheme 3 A *fac* → *mer* → *fac* isomerization sequence with a mixture of Ir(ppy)₃ and Ir(tpy)₃ does not lead to ligand scrambling.

mer-Ir(ppy)(tpy)₂ were not detected (ESI, Fig. S40†). In line with literature reports,^{11a} the photochemical *mer* → *fac* back-isomerization also proceeded without ligand scrambling.

Compounds, which can be cycled between two (meta)stable states **A** and **B**, are often referred to as ‘molecular switches’.¹⁷ Some applications of molecular switches rely on the geometric differences between the forms **A** and **B**. In order to demonstrate that large structural changes can be achieved with *fac* → *mer* isomerizations, we have prepared an Ir(C[^]N)₃ complex with a long 4-(2-pyridyl)-*p*-terphenyl ligand (tppy). The free ligand Htppy was obtained in 85% yield by Pd-catalyzed cross-coupling of 2-(4-bromophenyl)pyridine with 4-biphenylboronic acid. In analogy to a reported procedure,¹⁸ we then synthesized the chloro-bridged dimer [Ir(tppy)₂(μ-Cl)]₂ by reaction of Htppy with IrCl₃(H₂O)₃ in 2-ethoxyethanol-water (3 : 1) using microwave heating (150 °C, 20 min, yield: 82%, for details, see the ESI†). The homoleptic complex *mer*-Ir(tppy)₃ was obtained in 67% yield by reaction of [Ir(tppy)₂(μ-Cl)]₂ with Htppy and K₂CO₃ in glycerol at 200 °C (Scheme 4). Quantitative isomerization into *fac*-Ir(tppy)₃ was achieved by heating of a phenol solution of *mer*-Ir(tppy)₃ to 185 °C for 20 h.

Complex *fac*-Ir(tppy)₃ can be converted cleanly into the *mer* form using an acid-base treatment with TFA and NEt₃.



Scheme 4 Synthesis of *fac*- and *mer*-Ir(tppy)₃. The structures of the products are based on crystallographic analyses, with thermal ellipsoids at the 50% probability level. Hydrogen atoms are not shown for clarity.

Crystallographic analyses of the two isomers show the pronounced differences in geometry upon isomerization (Scheme 4). It is worth noting that a conversion of *mer*-Ir(tpy)₃ into *fac*-Ir(tpy)₃ was only achieved thermally, and not with light. Apparently, the bulky ligands inhibit the photochemical isomerization, which was suggested to involve the rupture of one Ir–N bond.^{13,14}

To study the stereoselectivity of the acid-base-induced *fac* → *mer* isomerization, we have prepared enantio-enriched *fac*-Ir(ppy)₃ by chromatographic separation (HPLC, Chiralpak IA column, for details, see the ESI†).¹⁹ Analysis of the sample before and after the TFA/NEt₃ treatment showed the same enantiomeric ratio of Δ : Λ = 83 : 17, implying that the *fac* → *mer* isomerization proceeds without racemization (Fig. 3a).²⁰

The high stereoselectivity indicates that the isomerization involves a selective reorientation of one of the three ppy ligands. Most likely, this reorientation occurs upon protonation. The protonated Hppy ligand needs to undergo an in-plane movement along with a 180° rotation around the Ir–N bond to give to pre-meridional form **I** (Fig. 3b). Base-induced Ir–C bond formation could then occur with minor structural rearrangements. This proposition is supported by the crystallographic analysis of the protonated complex [Ir(ppy)₂(Hppy)](NTf₂), which shows a pseudo-*mer* orientation of the three ligands and

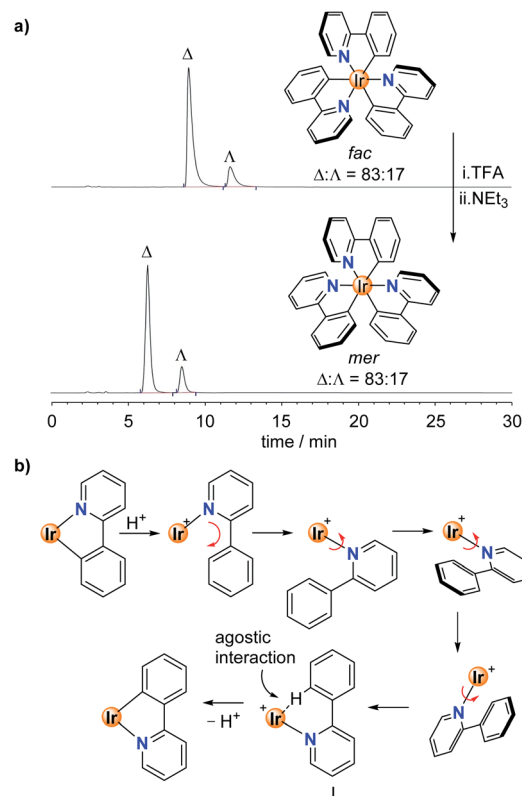
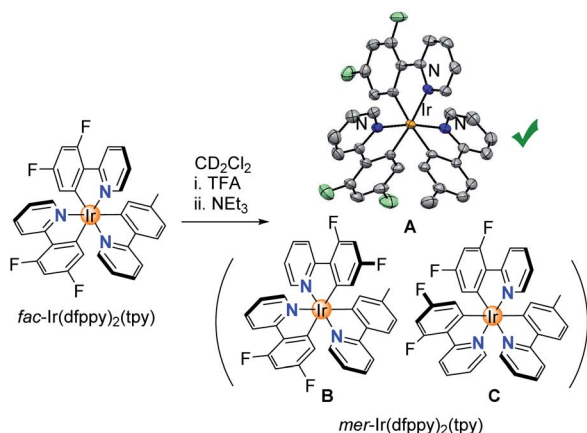


Fig. 3 (a) HPLC profile of a sample containing enantio-enriched *fac*-Ir(ppy)₃ before (top) and after (bottom) acid-base-induced *fac* → *mer* isomerization. (b) Plausible mechanism for the isomerization involving an in-plane movement of the protonated Hppy ligand and a 180° rotation around the Ir–N bond. A sequential movement–rotation is shown for illustrative purposes.



Scheme 5 Isomerization of *fac*-Ir(dfppy)₂(tpy) gives selectively complex A. The structure of the product is based on a crystallographic analysis, with thermal ellipsoids at the 50% probability level. Hydrogen atoms are not shown for clarity.

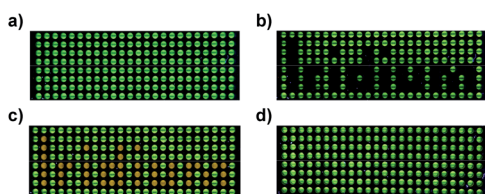


Fig. 4 Photos of a well plate filled with solutions of (a) *fac*-Ir(ppy)₃ in *o*-dichlorobenzene, (b) after addition of TFA to selected wells, (c) after addition of NEt₃ to the same wells, and (d) after irradiation with blue light. Details of the procedure are given in the ESI.†

an agostic interaction between the aromatic C–H group and the cationic Ir center (Fig. 1b). It is worth noting that the photochemical *mer* → *fac* back-isomerization proceeds *via* a different pathway, namely *via* Ir–N bond rupture¹⁴ rather than Ir–C bond rupture. Therefore, Ir(C^N)₃ complexes could be regarded as molecular motors performing a complex molecular motion.^{21,22}

Having established that homoleptic *fac*-Ir(C^N)₃ complexes can be isomerized chemically, we turned our attention to a heteroleptic complex, *fac*-Ir(dfppy)₂(tpy).²³ In principle, three different complexes could form during the chemically induced *fac* → *mer* isomerization (Scheme 5). Switching the orientation of the tpy ligand would give isomer A, whereas switching the orientation of one of the dfppy ligands would give isomer B or C. In view of the lower basicity of the fluorinated dfppy ligands, we anticipated that protonation of tpy would be preferred. Indeed, ¹H NMR spectroscopic analysis of a mixture of *fac*-Ir(dfppy)₂(tpy) and TFA (100 equiv.) in CD₂Cl₂ revealed that the more basic tpy ligand was protonated selectively (ESI, pages S88 and S89†). Subsequent ring closure with NEt₃ gave a single isomer, and a crystallographic analysis of the product revealed that isomer A had formed.

The possibility to interconvert *fac*- and *mer*-Ir(C^N)₃ complexes provides the opportunity to use these highly luminescent complexes for rewritable data storage devices.²⁴ As a proof-of-concept, we have used a well plate filled with *o*-

dichlorobenzene solutions of *fac*-Ir(ppy)₃ as a luminescent display. The text 'Iridium' was written chemically by addition of TFA (green-black contrast) and then NEt₃ (green-orange contrast), and reset was achieved by light (Fig. 4).

Conclusions

In conclusion, we have demonstrated that *fac*-Ir(C^N)₃ complexes can be converted cleanly into the thermodynamically less stable *mer* isomers by sequential treatment with first acid and then base. Spectroscopic and structural data indicate that the acid protonates a phenyl group of one ligand, resulting in Ir–C bond rupture. The intermediate protonated complex displays a *mer* arrangement of the N-donor atoms, priming the system for the kinetically controlled formation of *mer*-Ir(C^N)₃ in the presence of base. Notably, the structural rearrangement of the protonated HC^N ligand does not change the relative orientation of the two other C^N ligands. As a consequence, the isomerization is completely stereoselective, *i.e.* we observe conversion of *fac*-Δ into *mer*-Δ, and of *fac*-Λ into *mer*-Λ. The *mer* isomers can be converted back into the *fac* isomers by irradiation with light, and it is possible to perform multiple *fac* → *mer* → *fac* cycles with minor decomposition of the complexes.

fac-Ir(C^N)₃ and *mer*-Ir(C^N)₃ complexes are thermally highly stable, and the possibility to switch between these two stable forms opens up potential applications. One possible direction is rewritable data storage devices, and the luminescent display shown in Fig. 4 is a first proof-of-principle that such devices are feasible. Another possibility of the utilization of Ir(C^N)₃ complexes as geometric switches is in more complex nanostructures. The results obtained for Ir(tpy)₃ are evidence that large structural changes can be realized when converting *fac* isomers into *mer* isomers, and *vice versa*.

Finally, the results are also of interest from a synthetic point of view. Our new method allows preparing *mer* isomers of Ir(C^N)₃ complexes in a clean and fast fashion from the corresponding *fac* isomers. Notably, it is possible to access *mer* isomers, which are difficult to prepare otherwise. For example, the standard procedure to prepare the heteroleptic complex *mer*-Ir(dfppy)₂(tpy) gives isomer C (Scheme 5) rather than isomer A.^{11a,23}

Data availability

Raw data for this publication are available at Zenodo at: <https://zenodo.org/record/7002606#.YvympnaxUQ>.

Author contributions

A. Y. G. and K. S. initiated the study, A. Y. G. performed the experiments and analyzed the data, F. F.-T. collected and processed the X-ray data, A. R. performed the photophysical measurements, C. P. helped with the synthesis and the analysis of the heteroleptic Ir(dfppy)₂(tpy) complexes, and A. Y. G. and K. S. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 E. Zysman-Colman, *Iridium(III) in Optoelectronic and Photonics Application*, John Wiley & Sons, Chichester, West Sussex, 2017.
- 2 A. R. B. M. Yusoff, A. J. Huckaba and M. K. Nazeeruddin, *Top. Curr. Chem.*, 2017, **375**, 39.
- 3 P.-T. Chou and Y. Chi, *Chem. - Eur. J.*, 2007, **13**, 380–395.
- 4 M. H. Shaw, J. Twilton and D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898–6926.
- 5 R. C. McAtee, E. J. McClain and C. R. J. Stephenson, *Trends Chem.*, 2019, **1**, 111–125.
- 6 H. Shi, Y. Wang, S. Lin, J. Lou and Q. Zhang, *Dalton Trans.*, 2021, **50**, 6410–6417.
- 7 P.-Y. Ho, C.-L. Ho and W.-Y. Wong, *Coord. Chem. Rev.*, 2020, **413**, 213267.
- 8 D.-L. Ma, V. P.-Y. Ma, D. S.-H. Chan, K.-H. Leung, H.-Z. He and C.-H. Leung, *Coord. Chem. Rev.*, 2012, **256**, 3087–3113.
- 9 D. R. Martir and E. Zysman-Colman, *Chem. Commun.*, 2018, **55**, 139–158.
- 10 D. R. Martir and E. Zysman-Colman, *Coord. Chem. Rev.*, 2018, **364**, 86–117.
- 11 (a) A. R. McDonald, M. Lutz, L. S. von Chrzanowski, G. P. M. van Klink, A. L. Spek and G. van Koten, *Inorg. Chem.*, 2008, **47**, 6681–6691; (b) A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.*, 2003, **125**, 7377–7387.
- 12 For the targeted synthesis of *mer* Ir(C^N)₃ complexes, see: (a) A. Maity, B. L. Anderson, N. Deligonul and T. G. Gray, *Chem. Sci.*, 2013, **4**, 1175–1181; (b) S. Huo, J. C. Deaton, M. Rajeswaran and W. C. Lenhart, *Inorg. Chem.*, 2006, **45**, 3155–3157; (c) C.-H. Yang, K.-H. Fang, C.-H. Chen and I.-W. Sun, *Chem. Commun.*, 2004, 2232–2233.
- 13 D. Escudero, *ChemPhotoChem*, 2019, **3**, 697–701.
- 14 K. Tsuchiya, E. Ito, S. Yagai, A. Kitamura and T. Karatsu, *Eur. J. Inorg. Chem.*, 2009, **14**, 2104–2109.
- 15 T. Karatsu, T. Nakamura, S. Yagai, A. Kitamura, K. Yamaguchi, Y. Matsushima, T. Iwata, Y. Hori and T. Hagiwara, *Chem. Lett.*, 2003, **32**, 886–887.
- 16 M. Brookhart, M. L. H. Green and G. Parkin, *Proc. Natl. Acad. Sci.*, 2007, **104**, 6908–6914.
- 17 (a) J. D. Harris, M. J. Moran and I. Aprahamian, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 9414–9422; (b) W. Wang, Y.-X. Wang and H.-B. Yang, *Chem. Soc. Rev.*, 2016, **45**, 2656–2693; (c) B. L. Feringa and W. R. Browne, *Molecular Switches*, 2nd edn, Wiley-VCH, 2011.
- 18 B. Orwat, M. J. Oh, M. Zaranek, M. Kubicki, R. Januszewski and I. Kownacki, *Inorg. Chem.*, 2020, **59**, 9163–9176.
- 19 For the chiral separation of Ir(C^N)₃ complexes, see: (a) T.-Y. Li, Y.-M. Jing, X. Liu, Y. Zhao, L. Shi, Z. Tang, Y.-X. Zheng and J.-L. Zuo, *Sci. Rep.*, 2015, **5**, 14912; (b) F. J. Coughlin, M. S. Westrol, K. D. Oyler, N. Byrne, C. Kraml, E. Zysman-Colman, M. S. Lowry and S. Bernhard, *Inorg. Chem.*, 2008, **47**, 2039–2048; (c) X. Chen, Y. Okamoto, T. Yano and J. Otsuki, *J. Sep. Sci.*, 2007, **30**, 713–716.
- 20 The photochemical *mer* → *fac* isomerization of Ir(C^N)₃ complexes was reported to lead to partial racemization. See ref. 14.
- 21 For a discussion of the differences between molecular switches and molecular motors, see: (a) D. Datler, G. Fuks, J. Heiser, E. Moulin, A. Perrot, X. Yao and N. Giuseppone, *Chem. Rev.*, 2020, **120**, 310–433; (b) E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem.*, 2006, **119**, 72–196; *Angew. Chem., Int. Ed.*, 2007, **46**, 72–191.
- 22 For examples of chemically powered molecular motors, see: (a) S. Erbas-Cakmak, S. D. P. Fielden, U. Karaca, D. A. Leigh, C. T. McTernan, D. J. Tetlow and M. R. Wilson, *Science*, 2017, **358**, 340–343; (b) M. R. Wilson, J. Solà, A. Carlone, S. M. Goldup, N. Lebrasseur and D. A. Leigh, *Nature*, 2016, **534**, 235–240; (c) B. S. L. Collins, J. C. M. Kistemaker, E. Otten and B. L. Feringa, *Nat. Chem.*, 2016, **8**, 860–866; (d) G. Haberhauer, *Angew. Chem.*, 2011, **123**, 6539–6543; *Angew. Chem., Int. Ed.*, 2011, **50**, 6415–6418; (e) S. P. Fletcher, F. Dumur, M. M. Pollard and B. L. Feringa, *Science*, 2005, **310**, 80–82.
- 23 (a) J. Haribabu, Y. Tamura, K. Yokoi, C. Balachandran, M. Umezawa, K. Tsuchiya, Y. Yamada, R. Karvembu and S. Aoki, *Eur. J. Inorg. Chem.*, 2021, **18**, 1796–1814; (b) Y. Tamura, Y. Hisamatsu, S. Kumar, T. Itoh, K. Sato, R. Kuroda and S. Aoki, *Inorg. Chem.*, 2017, **56**, 812–833.
- 24 (a) H. Wang, X. Ji, Z. A. Page and J. L. Sessler, *Mater. Chem. Front.*, 2020, **4**, 1024–1039; (b) J. Andréasson and U. Pischel, *Isr. J. Chem.*, 2013, **53**, 236–246.

