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Letter

Influence of Fluorinated Substituents on the Near-Infrared Phosphorescence of 5d Metallocorroles

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Cite This: *ACS Org. Inorg. Au* 2023, 3, 241−245

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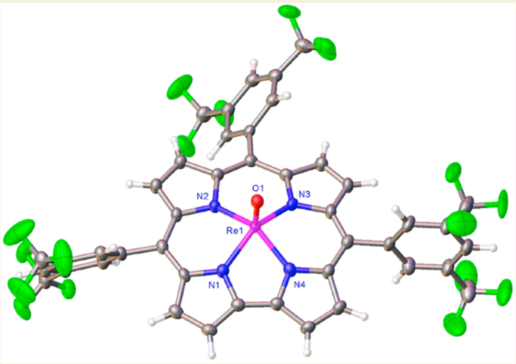
ABSTRACT: The influence of fluorinated substituents on the luminescent properties of rhenium-oxo, osmium-nitrido, and gold triarylcorroles was studied via a comparison of four ligands: triphenylcorrole (TPC), tris(*p*-trifluoromethylphenyl)corrole (T*p*CF$_3$PC), tris{3,5-bis(trifluoromethyl)-phenyl}corrole (T3,5-CF$_3$PC), and tris(pentafluorophenyl)corrole (TPFPC). For each metal series examined, fluorinated substituents were found to enhance the luminescent properties, with the phosphorescence quantum yields and triplet decay times increasing in the order TPC < T*p*CF$_3$PC < T3,5-CF$_3$PC < TPFPC. Among the 11 complexes examined, the highest phosphorescence quantum yield, 2.2%, was recorded for Re[TPFPC](O).

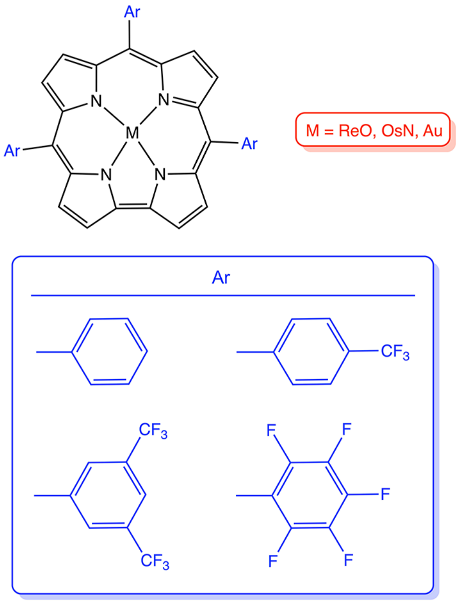


KEYWORDS: *Fluorinated compounds, fluorous, corrole, phosphorescence, triplet photosensitizer, gold, rhenium*

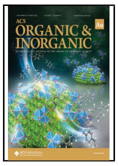
The last decade has witnessed the emergence of a unique class of transition metal complexes, the 5d metallocorroles.[1] Their uniqueness derives from their size-mismatched nature, which involves a large 5d ion encapsulated by a sterically constrained, macrocyclic corrole ligand.[2−4] In spite of the steric strain inherent in their structures, the middle and late 5d transition metal (Re,[5−8] Os,[9] Ir,[10] Pt,[11,12] and Au[13−20]) corroles have proved thermally and photochemically rugged. Furthermore, their photophysical properties are conducive to applications as photosensitizers, most notably in photodynamic therapy and oxygen sensing.[21−33] Interestingly, in the course of our photophysical studies on 5d metallotriarylcorroles, we observed somewhat higher phosphorescence quantum yields for tris{(*p*-trifluoromethyl)-phenyl}corrole complexes than for their more electron-rich counterparts.[24,28−30] The observation made us wonder whether fluorinated substituents might have a beneficial effect on the luminescence properties of 5d metallocorroles. A photophysical study was accordingly carried out on the complexes depicted in Chart 1, except for the M = OsN, Ar = C_6F_5 case, which was not studied because of synthetic difficulties. We found that fluorinated substituents indeed appear to have a beneficial effect on the luminescence properties of the complexes, significantly increasing both the phosphorescence quantum yields and the triplet decay times.

The influence of fluorinated substituents on the luminescence properties of rhenium-oxo, osmium-nitrido, and gold triarylcorroles was studied via a comparison of four ligands: triphenylcorrole (TPC), tris(*p*-trifluoromethylphenyl)corrole

Chart 1. Molecules Studied in This Work



Received: May 2, 2023
Revised: July 3, 2023
Accepted: July 5, 2023
Published: July 12, 2023



https://doi.org/10.1021/acsorginorgau.3c00016

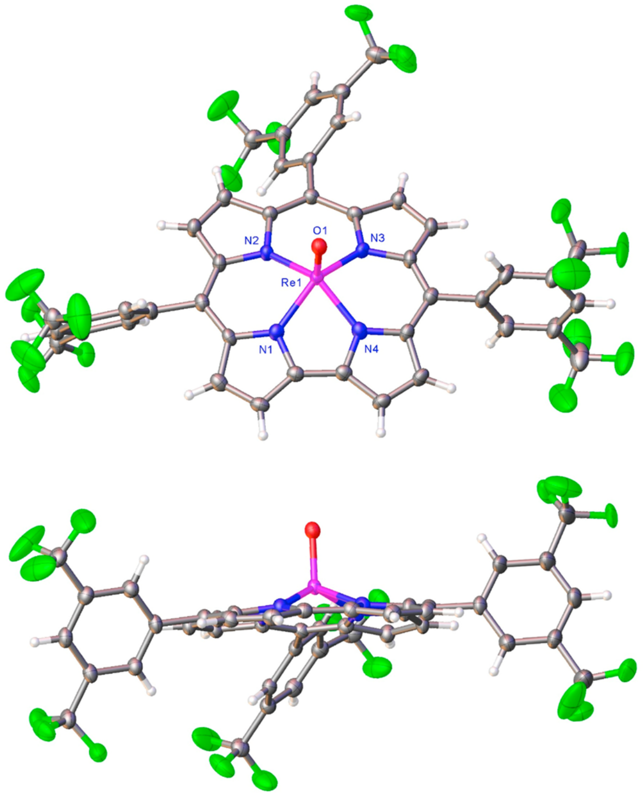


Figure 1. Two views of the thermal ellipsoid plot for Re[T3,5-CF$_3$PC](O) at 50% probability. Selected distances (Å): Re1−N1 1.992(3), Re1−N2 2.006(3), Re1−N3 2.015(3), Re1−N4 1.996(3), and Re1−O1 1.574(3) Å.

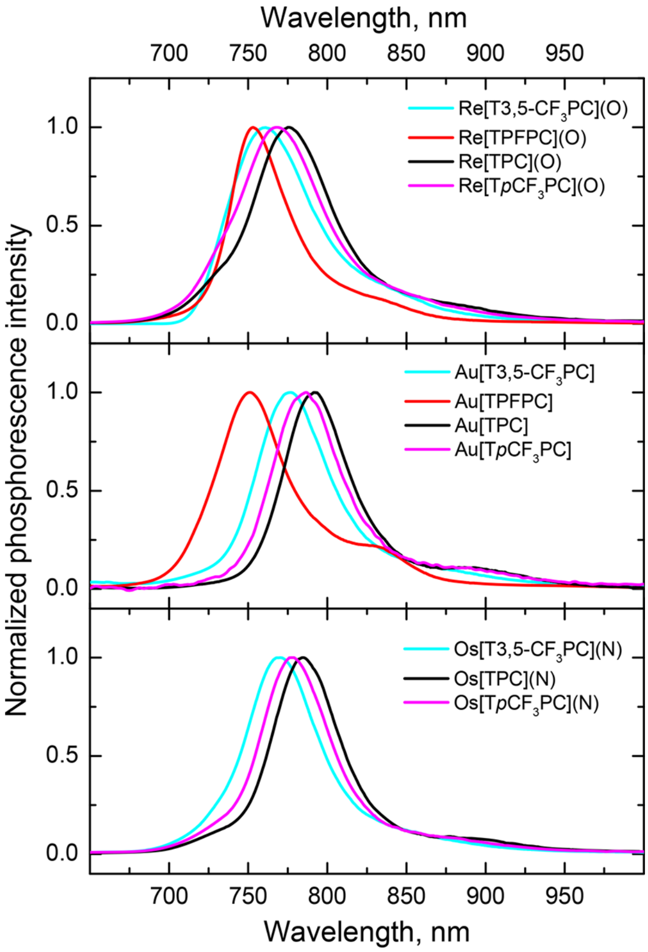


Figure 2. Emission spectra of the complexes in anoxic toluene at 23 °C. Excitation into the maximum of the Soret band of the complexes was performed.

(T*p*CF$_3$PC), tris{3,5-bis(trifluoromethyl)}corrole (T3,5-CF$_3$PC), and tris(pentafluorophenyl)corrole (TPFPC). The majority of the compounds in question have been previously synthesized;[5,9,15] four new compounds were synthesized specifically for this study, namely, Re[T3,5-CF$_3$PC](O), Os[T3,5-CF$_3$PC](N), Au[T3,5-CF$_3$PC], and Re[TPFPC](O). Unfortunately, Os[TPFPC](N) could not be synthesized because the azide used as part of the synthetic protocol resulted in nucleophilic displacement of the *para*-fluorines in the TPFPC ligand (consonant with multiple similar reactions in the literature[34−36]). Aside from that, the syntheses of the new compounds proved uneventful, and one, Re[T3,5-CF$_3$PC](O), yielded a single-crystal X-ray structure (Figure 1 and Table S1). Key photophysical and electrochemical properties of the compounds are listed in Table 1.

All of the complexes proved emissive in deoxygenated toluene at room temperature (Figure 2 and Table 1). The emission was efficiently quenched by molecular oxygen and is thus ascribed to phosphorescence. The absorption and excitation spectra (Figures S19−S23) proved virtually identical, indicating that the emission originates solely from the metal complexes while also confirming the purity of the

Table 1. Photophysical and Electrochemical Properties of ReO, OsN, and Au Triarylcorroles in Anoxic Toluene (23 °C)

complex	λ_{max} abs, nm	$\lambda_{max\text{-}phos}$ (nm)	Φ_{phos} (%)	τ_{phos} (μs)	$E_{1/2,ox1}$ (V)	$E_{1/2,red1}$ (V)	$E_{1/2,red2}$ (V)	ref
Re[TPC](O)	440, 554, 586	776(770)[a]	1.2	60	0.98	−1.26		5, 29
Re[T*p*CF$_3$PC](O)	440, 553, 586	768(777)[a]	1.4 (1.5)[a]	74	1.10	−1.16		5, 29
Re[T3,5-CF$_3$PC](O)	440, 553, 586	760	1.6	75	1.21	−1.11	−1.64	this work
Re[TPFPC](O)	437, 552, 586	753	2.2	99	1.31	−1.04	−1.68	this work
Os[TPC](N)	444, 554, 595	784	0.64 (0.54)[b]	125(128)[c]	0.91	−1.28		9, 24
Os[T*p*CF$_3$PC](N)	444, 554, 593	778	0.7 (0.54)[b]	139(150)[c]	1.02	−1.19		9, 24
Os[T3,5-CF$_3$PC](N)	443, 553, 588	770	0.81	155	1.12	−1.10	−1.62	this work
Au[TPC]	421, 494, 532, 561, 575	792	0.23 (0.18)[d]	94(86)[d]	0.80	−1.38		15
Au[T*p*CF$_3$PC]	423, 494, 532, 562 (sh), 575	786	0.26 (0.19)[d]	97(98)[d]	0.94	−1.29		15
Au[T3,5-CF$_3$PC]	421, 493, 529, 567	777	0.33	99	1.05	−1.19	−1.62	this work
Au[TPFPC]	415, 491, 527, 561	751	0.68	170	1.18	−1.11	−1.68	this work

[a] Ref 29; excitation in the Q-band. [b] Ref 24; the Φ_{phos} values have been recalculated based on the corrected value (21%) for the standard platinum(II) tetraphenyltetrabenzoporphyrin (Pt[TPTBP]).[37] [c] Ref 24; frequency domain measurement. [d] Ref 23.

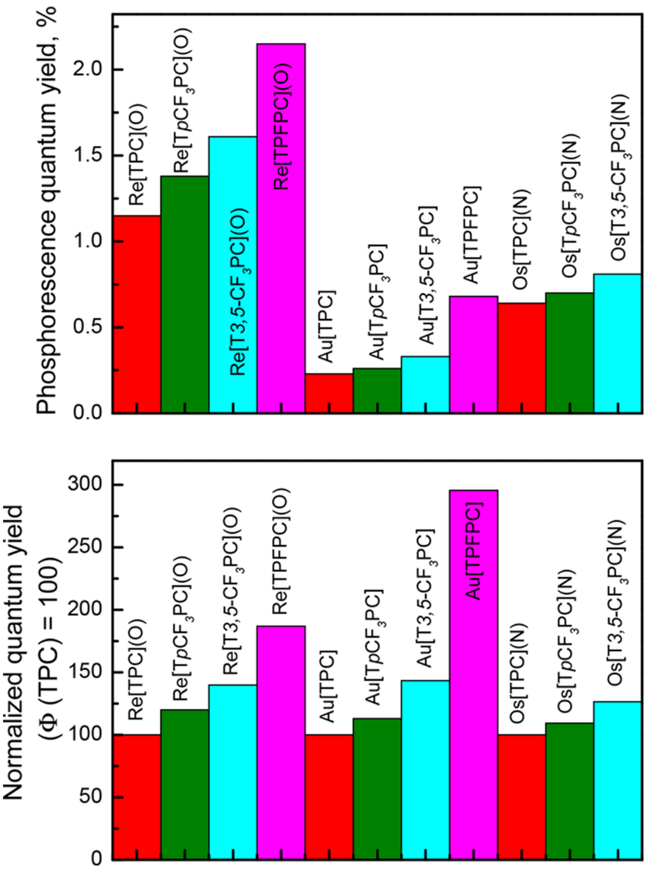


Figure 3. Phosphorescence quantum yields of the ReO, OsN, and Au corroles. The lower plot depicts the enhancement of the quantum yield upon fluorination: the values are normalized for the quantum yields of the TPC complex of each metal; i.e., the Φ_{phos} values of Re[TPC](O), Os[TPC](N), and Au[TPC] are each set as 100%.

compounds. Although the emission spectra of the T3,5-CF$_3$PC and TPFPC complexes are generally similar to those of the previously studied TPC and T*p*CF$_3$PC complexes (which were also remeasured in this study), the emission maxima were found to shift hypsochromically with increasing electron-withdrawing character of the *meso*-aryl substituents; this effect was observed for all three metal series examined.

As shown in Table 1, fluorination results in an increase in both luminescence quantum yields and decay times in the order TPC < T*p*CF$_3$PC < T3,5-CF$_3$PC < TPFPC, which is also the order of the redox potentials (see Figures S9−S13 for selected cyclic voltammograms). Figure 3 presents a graphical representation of the quantum yields for the different complexes. The ReO complexes are by far the strongest emitters, followed by the OsN, and last by the Au (Figure 3, upper panel). Notably, compared with their TPC analogues, the luminescence of Au[TPFPC] is enhanced much more strongly than that of Re[TPFPC](O) (Figure 3, lower panel). Thus, whereas the phosphorescence quantum yield triples on going from Au[TPC] to Au[TPFPC], the enhancement is less than double for their ReO counterparts. As a result of the fluorination-mediated enhancement, Au[TPFPC] emits as efficiently as Os[TPC](N). The trend in the luminescence decay times parallels that observed for the luminescence quantum yields (Table 1). The decay time of Au[TPFPC] is thus much longer (170 μs) than that of the other Au triarylcorroles (94−99 μs). Interestingly, although the parallelism is far from exact, the present findings appear similar to those of Liu and co-workers, who observed fluorination-induced enhancements of triplet quantum yields for free-base and gallium triarylcorroles.[38]

The fact that the order of phosphorescence quantum yields parallels the order of redox potentials for each of three series of 5d metallocorroles suggests that the mechanism of enhanced luminescence is largely electronic in origin. However, the *ortho* fluorines in the TPFPC complexes may confer some degree of conformational rigidity, leading to increased triplet lifetimes. Fluorination also has a major impact on solute−solvent interactions, which, in turn, may also affect the luminescence properties. At this point, these potential influences remain to be disentangled, and the striking impact of fluorination is simply presented as an empirical observation.

In conclusion, introduction of fluorinated substituents onto the *meso*-phenyl groups results in enhancement of the luminescence properties of all three series of 5d metallocorroles: ReO, OsN, and Au. Substitution of phenyl groups by pentafluorophenyl groups leads to the highest increase in the luminescence quantum yields and decay times. This enhancement is particularly strong in the case of the Au corroles, where the phosphorescence quantum yield triples on going from Au[TPC] to Au[TPFPC]. An intriguing question concerns whether peripheral fluorination might have a similar positive effect on the luminescence properties of other porphyrin-type complexes such as true porphyrins, carbaporphyrins, hydroporphyrins, and dipyrrin derivatives. Time will tell.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsorginorgau.3c00016.

Experimental methods, ^{1}H and ^{19}F NMR spectra, electrospray ionization mass spectra, optical spectra, and additional photophysical data (PDF)

Accession Codes

CCDC 2247280 contains 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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Author Contributions

CRediT: **Krister Engedal Johannessen** data curation (equal), investigation (equal), methodology (equal), writing-original draft (supporting); **Martin Amund Langaas Johansen** investigation (supporting), methodology (supporting), writing-original draft (supporting); **Rune F. Einrem** investigation (supporting), methodology (supporting), writing-original draft (supporting); **Laura J. M^{c}Cormick M^{c}Pherson** investigation (equal), methodology (equal), writing-original draft (supporting); **Abraham B. Alemayehu** formal analysis (lead), investigation (lead), methodology (lead), supervision (lead), writing-original draft (lead); **Abhik Ghosh** conceptualization (lead), formal analysis (lead), project administration (lead), resources (lead), supervision (lead), writing-original draft (lead), writing-review & editing (lead); **Sergey M. Borisov** formal analysis (lead), investigation (lead), methodology (lead), resources (lead), validation (lead), writing-original draft (lead), writing-review & editing (lead).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported in part by the Research Council of Norway (grant no. 262229 to A.G.). The UK National Crystallography Service, supported by grant no. EP/W02098X/1 from the EPSRC, is also gratefully acknowledged.

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