

RSC Advances



This article can be cited before page numbers have been issued, to do this please use: W. Chen, J. Zhang, J. Mack, G. Kubheka, T. Nyokong and Z. Shen, *RSC Adv.*, 2015, DOI: 10.1039/C5RA07250F.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Corrole-BODIPY Conjugates: Enhancing the Fluorescence and Phosphorescence of the Corrole Complex via Efficient Through Bond Energy Transfer

Wei Chen,^a Jianfeng Zhang,^b John Mack,^{c,*} Gugu Kubheka,^c Tebello Nyokong^c and Zhen Shen^{a,*}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

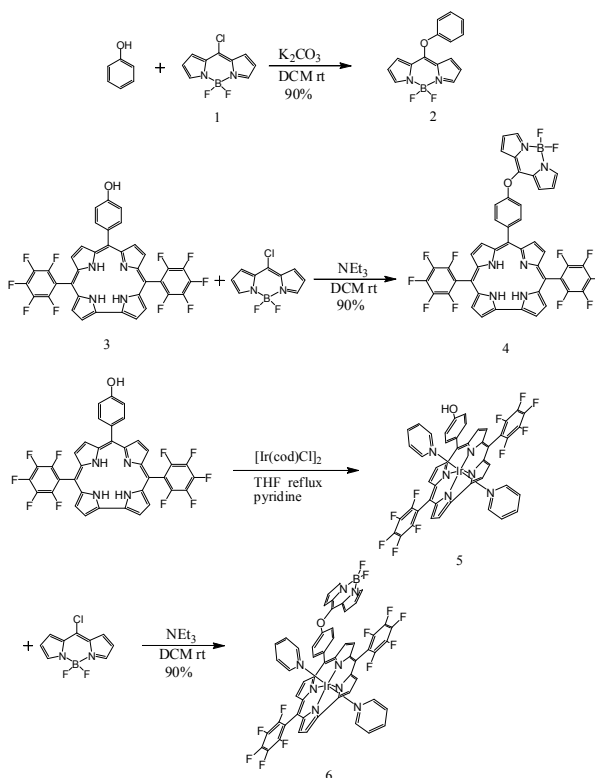
www.rsc.org/

New corrole-BODIPY conjugates have been synthesized in high yield under mild conditions. Upon excitation at the absorption maximum of the BODIPY antenna chromophore, the fluorescence intensity of the free base corrole-BODIPY conjugate increases by ca. 300%, and significant phosphorescence intensity is observed for the iridium(III) complex of the conjugate, while almost no phosphorescence is observed for the parent iridium(III) corrole, due to through-bond energy transfer from the BODIPY antenna-chromophore to the corrole core.

Introduction

There is considerable interest in the design of dye-sensitized and organic photovoltaic cells. One of the most popular approaches is to synthesize core-shell systems, which are comprised of antenna chromophores linked to a core chromophore. Ideal candidates for this should absorb strongly in 500–800 nm region with the antenna chromophores transferring excitons to the central chromophore.¹ Recently, porphyrin-BODIPY (BODIPY = boron dipyrromethene) conjugates have gained considerable attention, due to favourable photophysical properties, such as very high fluorescence quantum yields, and their other potential applications, such as their use as fluorescent probes.² Porphyrin derivatives have intense absorption bands in the UV-visible region with high molar absorption coefficients, with the exception of the blue-green region of solar spectrum (450–550 nm).³ Since BODIPYs usually have intense absorption bands in the blue-green region,⁴ as well as other desirable photochemical and photophysical properties, the two chromophores can be viewed as being complementary in terms of the solar spectrum, making their conjugates suitable for solar cell applications.

Corroles are porphyrin derivatives that contain a direct pyrrole-pyrrole bond and have broadly similar chemical properties, but are better suited to stabilizing the higher



Scheme 1 Synthetic procedures for corrole-BODIPY conjugates 4 and 6.

oxidation states of a central metal ion, since the ligand π -system is trianionic. To the best of our knowledge, there has only been one example of a corrole-BODIPY conjugate reported previously.⁵ Herein, we report a facile and high-yield synthesis of a corrole-BODIPY conjugate and its iridium(III) complex, Scheme 1, in order to study the impact of the BODIPY antenna chromophore on the properties of the core corrole π -system. The *meso*-halogenated BODIPY 1 was synthesized

^a State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China.

^b The Second People's Hospital of Nanjing, Nanjing 210003, China.

^c Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa.

† Electronic Supplementary Information (ESI) available: methods and synthesis, MS data and ¹H and ¹³C NMR spectra, and additional experimental and calculated optical spectra. See DOI: 10.1039/x0xx00000x

according to literature procedures,⁶ and corrole **3** was synthesized using the general method for A2B corroles.⁷ **1** reacts readily with phenol under mild conditions to form **2** in high yield. In a similar manner, corrole **3** and its iridium complex **5**, which contain a phenol moiety at the *meso*-position, also readily react with the *meso*-halogenated BODIPY **1** to form **4** and **6**, respectively, in high yield. Full characterization data are provided in the ESI.

Results and Discussion

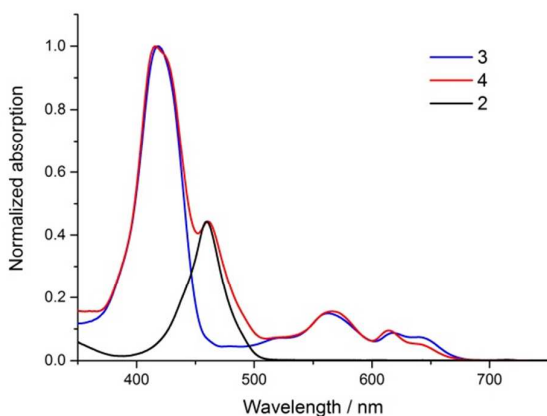


Fig. 1 Normalized absorption spectra of **2** (black), **3** (blue) and **4** (red) in toluene at room temperature.

The normalized UV-visible absorption spectra of **2-4** are shown in Figure 1. The absorption spectrum of corrole-BODIPY conjugate **4** has two intense bands at 415 (log $\epsilon = 4.78$) and 460 (log $\epsilon = 4.73$) nm, and is almost identical to the sum of the spectra of corrole **3** and BODIPY **2** in this regard, Table 1. These observations clearly demonstrate that there is no significant ground-state interaction between the two chromophores.⁸ Peaks associated with the BODIPY and corrole moieties of **4** can also be readily identified by magnetic circular dichroism (MCD) spectroscopy (Figure 2), since the absence and presence of a cyclic perimeter results in very weak and very intense MCD signals, respectively.

The optical spectroscopy of corroles can be described in terms of perturbations to an $M_L = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6, \pm 7$ sequence of MOs associated with the parent $C_{15}H_{15}^{3-}$ perimeter for the 15 atom 18 π -electron system of the inner ligand perimeter.⁹ Michl¹⁰ demonstrated that when the symmetry of aromatic and heteroaromatic π -systems are lowered by perturbations to the structure, the alignments of the nodal patterns of the four frontier π -MOs of the parent perimeter are retained. The HOMO and LUMO of the parent $C_{15}H_{15}^{3-}$ perimeter for corroles have $M_L = \pm 4$ and ± 5 nodal properties, respectively. By analogy with Gouterman's 4-orbital model¹¹ it can be demonstrated that this leads to allowed B (or Soret) and forbidden Q bands based on allowed $\Delta M_L = \pm 1$ and forbidden $\Delta M_L = \pm 9$ transitions. Michl introduced an *a*, *s*, *-a* and *-s* nomenclature for MOs whether there is a nodal plane (*a* and *-a*) or antinodes (*s* and *-s*) aligned

Table 1 Absorption and luminescence data (nm) for **2-6** measured at room temperature in aerated and degassed toluene solutions for fluorescence and phosphorescence, respectively, and fluorescence (Φ_F) and phosphorescence (Φ_{Ph}) state lifetimes (τ^{air}) and quantum yield values obtained upon excitation at 416 and 460 nm and standardized against tetraphenylporphyrin ($\Phi_F = 0.13$ in toluene solution at 298 K).¹⁸

λ_{abs} (log ϵ)	λ_{em}	Φ_F 416 nm	Φ_F 460 nm	$\tau^{air}/$ ns	Φ_{Ph} 416 nm	Φ_{Ph} 460 nm	$\tau^{air}/$ μs
2 461(4.73)	502	---	96%	6.45	---	---	---
3 416 (4.78)	662	11.3%	6%	4.44	---	---	---
4 415 (4.78) 460 (4.73)	658	11.6%	18%	3.57	---	---	---
5 416 (4.26)	662, 830	0.77%	---	8.47	0.32%	---	1.86
6 415 (4.23) 460 (4.15)	657, 830	0.77%	1.11%	4.22	0.36%	0.52%	1.78

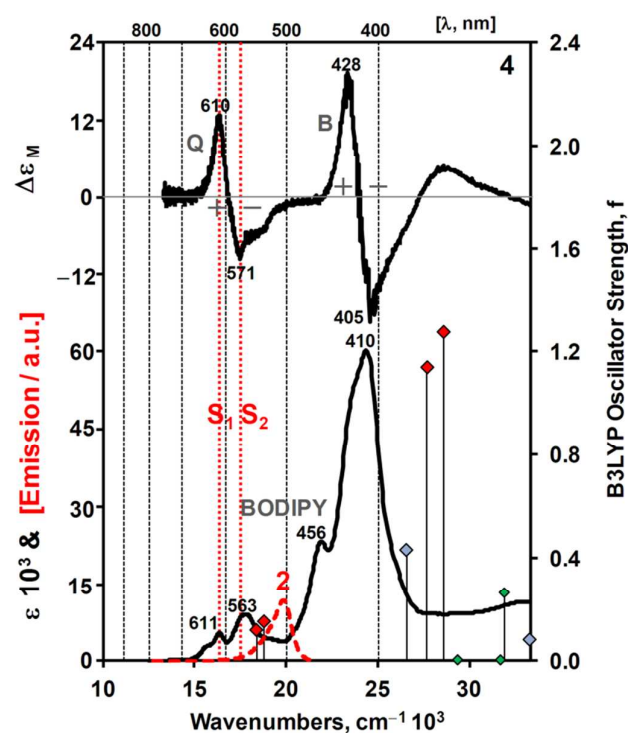


Fig. 2 Absorption and MCD spectra of **4** in toluene at room temperature. A TD-DFT calculation calculated for the B3LYP geometry of **4** by using the CAM-B3LYP functional with 6-31G(d) basis sets, is plotted against a secondary axis. Large red and blue diamonds are used to denote $\pi \rightarrow \pi^*$ bands associated with the corrole and BODIPY moieties, respectively. Green diamonds denote bands with charge transfer character between different π -system moieties. The sign sequence of the Faraday $\Delta\epsilon$ terms associated with the Q and B bands of the corrole π -system is highlighted using the conventions of Piepho and Schatz.¹⁸ The details of the TD-DFT calculation are provided in Table S1 in ESI. The fluorescence emission band of **2** is plotted against an arbitrary axis to demonstrate the lack of significant overlap with relatively narrow electronic absorption bands associated with the S_1 and S_2 states, which can be readily identified by comparison with the MCD spectrum.

bands of **4** at 611, 563 and 410 nm, while there is a near complete absence of MCD intensity at 456 nm, so the band

can hence be readily assigned to the main BODIPY absorption band (Figure 2). The results of a TD-DFT calculation carried out on a B3LYP optimized geometry of **4** using the CAM-B3LYP functional with 6-31G(d) basis sets are consistent with this assignment (Table S1 in ESI). The MCD spectra of free base with the γ -axis of the corrole π -system (Figure 3).¹⁰

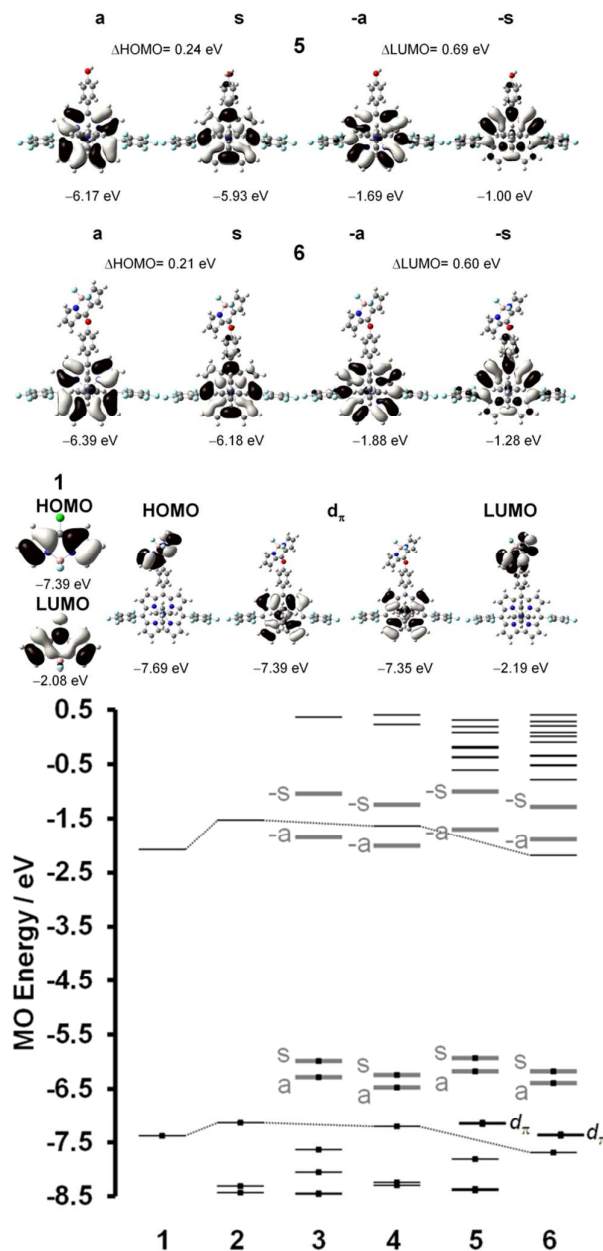


Fig. 3 Angular nodal patterns for the frontier MOs of **1**, **5** and **6** at an isosurface of 0.02 a.u. (TOP). MO energies of **1-6** in TD-DFT calculations for B3LYP geometries carried out using 6-31G(d) basis sets for **1-4** and SDD basis sets for **5** and **6**. Occupied MOs are denoted with small black square. The four frontier π -MOs associated with Michl's perimeter model¹⁰ for a $C_{15}H_{15}^{3-}$ parent hydrocarbon perimeter are highlighted in light gray and are labeled using Michl's a , s , $-a$ and $-s$ MOs nomenclature. The $5d$ orbitals associated with the Ir(III) ions of **5** and **6** are offset to the right. Dotted lines are used to highlight trends in the energies of the HOMO and LUMO of the BODIPY π -system.

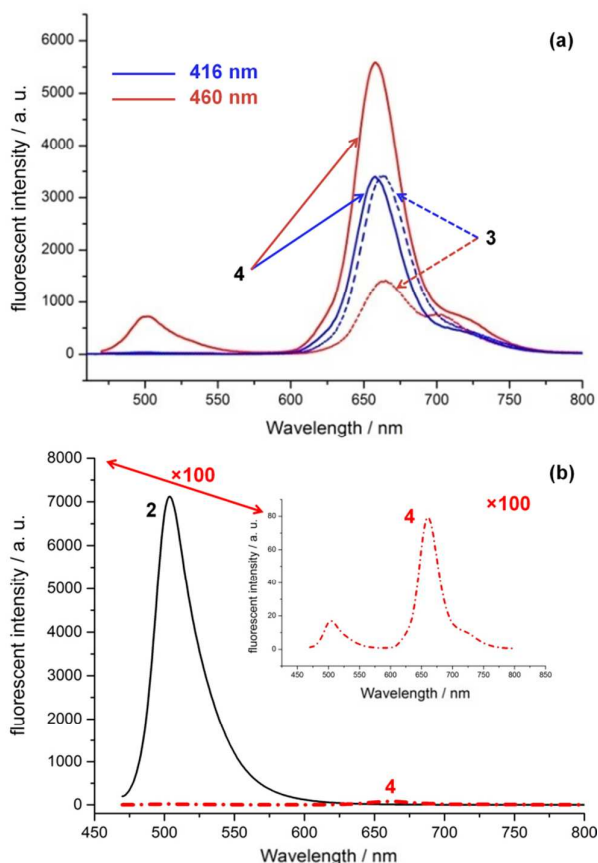


Fig. 4 (a) Emission spectra of **4** (solid line) and **3** (dashed line) in aerated toluene at room temperature. The blue lines are fluorescence spectra measured upon excitation at 416 nm, while the red lines are for excitation at 460 nm. The solutions of **3** ($1.23 \times 10^{-6} M^{-1}$) and **4** ($1.23 \times 10^{-6} M^{-1}$) have the same optical density at 416 nm. (b) Fluorescence spectra of **2** and **4** upon excitation at 460 nm in toluene at room temperature. The solutions of **2** ($1.21 \times 10^{-6} M^{-1}$) and **4** ($1.23 \times 10^{-6} M^{-1}$) have the same optical density at 460 nm.

Intense coupled pairs of Faraday Φ_0 are observed for the Q and B triarylcorroles exhibit an $+/-/+/-$ sign sequence in the Q and B bands in ascending energy terms (Figure S7).^{9a,12} This can be readily explained by the significant lifting of the degeneracy of the LUMO of the porphyrin π -system when a *meso*-carbon is removed (Figure 3). Michl has demonstrated that a $+/-/+/-$ sequence is observed when the splitting of the MOs derived from the $1e_g^*$ porphyrin LUMO (referred to as the Δ LUMO value, for the energy gap between the $-a$ and $-s$ MOs) is greater than that of the MOs derived from the occupied $1a_{1u}$ and $1a_{2u}$ frontier π -MOs of the porphyrin π -system (referred to as the Δ HOMO value for the energy gap between the a and s MOs).¹⁰

Toluene solutions of **3** and **4** were excited at 416 nm (in the B band of the corrole π -system) and 460 nm (the absorption maximum of the BODIPY chromophore), respectively, to study the energy transfer between the antenna chromophore and the corrole ligand (Figure 4). Upon excitation at 416 nm, the emission spectra of both **3** and **4** contains one band at ca. 662 nm, in the region where fluorescence is typically observed for

corroles. It should be noted, that **4** has almost the same fluorescence intensity as **3**, but there is a slight hypsochromatic shift, Table 1, due to the different *meso*-substituent. In contrast, upon excitation at 460 nm, two emission bands are observed for conjugate **4**. A band centered at ca. 500 nm is associated with the emission from the BODIPY antenna complex, while the emission band for the corrole chromophore lies at ca. 662 nm. The fluorescence intensity from the S_1 state of the corrole is stronger than that obtained by direct excitation of the corrole core π -system at 416 nm. These observations indicate that part of the energy absorbed by the BODIPY donor moiety is transferred to the corrole π -system.

Upon excitation at 460 nm the fluorescence spectrum for an equimolar mixture of **2** and **3** contains no significant corrole emission band at 662 nm (Fig. S8, ESI). Evidence for significant excited state energy-transfer is only observed when a BODIPY antenna moiety is linked to a corrole core through a covalent aryl C–O bond. This results in a three-fold enhancement of the fluorescence quantum yield (Table 1), which makes the conjugate potentially suitable for use in solar cells. A significant contribution from Förster resonance energy transfer (FRET) is not likely in this context, since there is very limited overlap between the emission band of BODIPY **2** at 502 nm and the main electronic band associated with the S_1 state in the Q band region of the spectrum of conjugate **4** (Fig. 2).

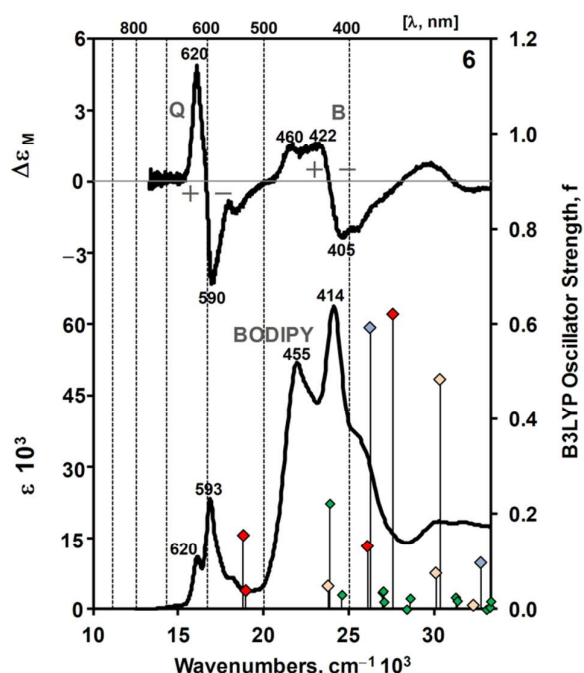


Fig. 5 Absorption and MCD spectra of **6** in toluene at room temperature. A TD-DFT calculation calculated for the B3LYP geometry of **6** by using the CAM-B3LYP functional with SDD basis sets, is plotted against a secondary axis. Large orange, red, and blue diamonds are used to denote metal-to-ligand charge transfer bands and $\pi \rightarrow \pi^*$ bands associated with the corrole and BODIPY moieties, respectively. Green diamonds denote bands with charge transfer character between different π -system moieties. The sign sequence of the Faraday $\Delta\epsilon$ terms associated with the Q and B bands of the corrole π -system is highlighted using the conventions of Piepho and Schatz.²⁰ The details of the TD-DFT calculation are provided in Table S1 in ESI.

If the energy is transferred primarily through the chemical bonds rather than through space, it depends on a mechanism which is known as through-bond energy transfer (TBET). Although there is no direct conjugation between the *meso*-phenyl substituent of the porphyrin and BODIPY moieties, there is scope for the lone pair orbitals of the linking oxygen atoms to interact with the two π -systems. For example, the recent spectroscopic characterization and theoretical analysis of a novel nickel 10-oxacorrole complex by Kobayashi and co-workers demonstrated that an sp^3 hybridized oxygen atom can form part of a cyclic π -system with properties very similar to those of a conventional 18- π -electron heteroaromatic π -system of a porphyrinoid ligand.¹³ Using the commonly used formula for energy transfer: $100 \times [1 - (\text{fluorescence intensity of the donor in the conjugate}) / (\text{fluorescence intensity of the free donor})]\%$,¹⁵ the energy transfer efficiency for the TBET process is estimated to be ca. 99%. Otsuki et al have demonstrated that effective TBET can be mediated even when the bond is noncovalent.¹⁴ It is noteworthy that upon excitation at 460 nm, the fluorescence intensity of **4** at 502 nm is two orders of magnitude weaker than that of BODIPY **2**, Figure 4. This is what would normally be anticipated, however, since deactivation of the S_1 state is also likely to occur *via* nonradiative decay.¹⁶

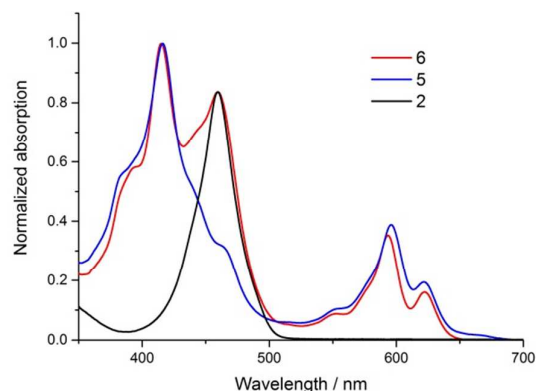


Fig. 6 Normalized absorption spectra of **2** (black), **5** (blue) and **6** (red) in toluene at ambient temperature.

Iridium porphyrins and their analogues have significantly different photophysical properties from those of other porphyrin complexes, since they phosphoresce in the NIR region.¹⁷ The phosphorescent intensity is strongly dependent on the nature of the axial ligand, and the highest phosphorescence quantum yields are reported to be only ca. 1%,¹⁸ which makes them relatively unsuitable for use in organic light-emitting diodes. The presence of a BODIPY antenna chromophore can potentially enhance the intensity of the NIR region luminescence. The Ir(III) corrole-BODIPY conjugate **6** was found to emit beyond 800 nm (Table 1). The absorption spectrum of **6** is almost identical to the sum of the spectra of **5** and **2**. The MCD spectroscopy and TD-DFT calculations of **6** are broadly similar to those of **4** (Figure 5) in terms of the energies of the Q and B bands of the corrole π -system and the main BODIPY absorption band, since the energies of the frontier π -MOs are largely unaffected by the

presence of the central diamagnetic Ir(III) ion (Figure 3). The presence of the $5d_{xz}$ and $5d_{yz}$ (d_{π}) orbitals close in energy to the **a** and **s** MOs of the corrole π -system enhances configurational interaction between states associated with the porphyrin and BODIPY moieties (Table S1 in ESI), so there is significant MCD intensity between the Q and B band regions (Figure 5), in contrast with what is observed in the spectrum of **4** (Figure 3). In the NIR region (Figure 7), the phosphorescence emission intensity is clearly stronger upon excitation at the

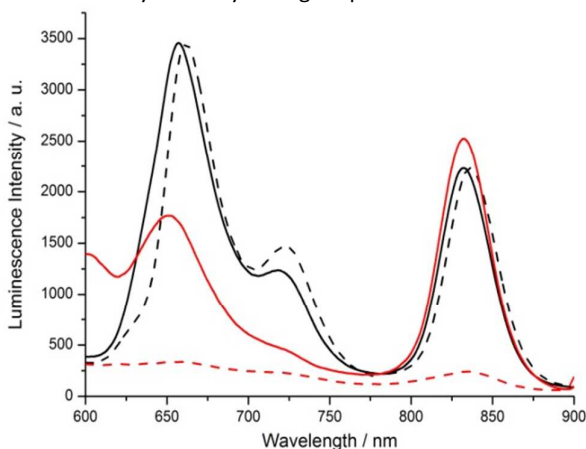


Fig. 7 Solid and dashed lines are used for the emission spectra of **6** and **5**, respectively, in toluene at room temperature, while black and red lines denote excitation at 416 and 460 nm, respectively. The measurements were made on solutions of **5** ($1.35 \times 10^{-6} \text{ M}^{-1}$) and **6** ($1.36 \times 10^{-6} \text{ M}^{-1}$) with the same optical density at 416 nm.

absorption band maximum of the BODIPY antenna, due to efficient energy transfer from the BODIPY antenna chromophore to the iridium(III) corrole core. The slight decrease in lifetime of **6** compared to **5** (Table 1) is consistent with the presence of a nonradiative process associated with the incorporation of a flexible antenna chromophore chain.¹⁹

Conclusions

A corrole-BODIPY conjugate and its iridium(III) complex have been prepared under mild conditions in high yield, so that the luminescence enhancement in such core-shell systems can be assessed. The efficient excited state energy transfer from the BODIPY antenna chromophore to the core corrole π -system, results in an enhancement of the fluorescent intensity of the corrole by 300%, while the phosphorescent intensity of the iridium(III) corrole-BODIPY conjugate is also increased markedly, making them potentially suitable for applications in solar cells and OLEDs.

Acknowledgements

Financial support was provided by the Major State Basic Research Development Program of China (Grant Nos. 2013CB922101 & 2011CB808704), the National Natural Science Foundation of China (No. 21371090), the Natural Science Foundation of Jiangsu Province (BK20130054) to ZS,

the China-South Africa joint research program (CS08-L07) to ZS and JM and an NRF CSUR grant (93627) to JM. The theoretical calculations were carried out at the Centre for High Performance Computing in Cape Town.

Notes and references

- (a) M. R. Wasielewski, *J. Org. Chem.*, 2006, **71**, 5051. (b) S. Fukuzumi, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2283.
- M. T. Whited, P. I. Djurovich, S. T. Roberts, A. C. Durrell, C. W. Schlenker, S. E. Bradforth and M. E. Thompson, *J. Am. Chem. Soc.*, 2010, **133**, 88.
- (a) L. Lin and E. W. Diau, *Chem. Soc. Rev.*, 2013, **42**, 1921-1933. (b) F. Li, S. L. Yang, Y. Ciringh, J. Seth, C. H. Martin, D. L. Singh, D. Kim, R. R. Birge, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Am. Chem. Soc.*, 1998, **120**, 10001.
- (a) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891. (b) H. Lu, J. Mack, Y. C. Yang and Z. Shen, *Chem. Soc. Rev.*, 2014, **43**, 4778. (c) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem. Int. Ed.* 2008, **47**, 1184. (d) N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.* 2012, **41**, 1130. (e) Z. Shen, H. Röhr, K. Rurack, H. Uno, M. Spieles, B. Schulz, G. Reck and N. Ono, *Chem. Eur. J.* 2004, **10**, 4853.
- B. Brizet, N. Desbois, A. Bonnot, Adam. Langlois, J. Barbe, A. Dobois, C. P. Gros, C. Goze, F. Denat and P. D. Harvey, *Inorg. Chem.*, 2014, **53**, 3392.
- (a) V. Leen, P. Yuan, L. Wang, N. Boens and W. Dehaen, *Org. Lett.*, 2012, **24**, 6150.
- (a) D. T. Gryko and K. Jadach, *J. Org. Chem.*, 2001, **66**, 4267. (b) M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2405.
- J. Y. Liu, E. A. Ermilov and D. K. P. Ng, *Chem Comm.*, 2009, 1517.
- (a) X. Liang, J. Mack, L. Zheng, Z. Shen and N. Kobayashi, *Inorg. Chem.*, 2014, **53**, 2397. (b) J. Mack, M. Bunya, D. Lansky, D. P. Goldberg, N. Kobayashi, *Heterocycles* 2008, **76**, 1369.
- (a) J. Michl, *J. Am. Chem. Soc.* 1978, **100**, 6801. (b) J. Michl, *J. Am. Chem. Soc.* 1978, **100**, 6812. (c) J. Michl, *Pure Appl. Chem.* 1980, **52**, 1549. (d) J. Michl, *Tetrahedron* 1984, **40**, 3845.
- M. Gouterman, In *The Porphyrins*; D. Dolphin, Ed.; Academic Press: New York, 1978; Vol. III, Part A, pp 1-165.
- C. J. Ziegler, J. R. Sabin, G. R. Geier and V. N. Nemykin, *Chem Comm.*, 2012, **48**, 4743.
- T. Ito T, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi and H. Shinokubo, *Angew. Chem. Int. Ed.*, 2012, **51**, 8542.
- J. Otsuki, Y. Kanazawa, A. Kaito, D.-M. S. Islam, Y. Araki, and O. Ito, *Chem. Eur. J.*, 2008, **14**, 3776.
- (a) G. S. Jiao, A. Loudet, H. B. Lee, S. Kalinin, L. B. Johanssonb, K. Burgess, *Tetrahedron*, 2003, **59**, 3109; (b) M. D. Yilmaz, O. A. Bozdemir, E. U. Akkaya, *Org. Lett.*, 2006, **8**, 2871.
- M. Y. Berezin and S. Achilefu, *Chem. Rev.*, 2010, **110**, 2641.
- (a) J. H. Palmer, M. W. Day, A. D. Wilson, L. M. Henling, Z. Gross and H. B. Gray, *J. Am. Chem. Soc.*, 2008, **130**, 7786. (b) J. H.

COMMUNICATION

Journal Name

- Palmer, A. Mahammed, K. M. Lancaster, Z. Gross and H. B. Gray, *Inorg. Chem.*, 2009, **48**, 9308.
- 18 J. H. Palmer, A. C. Durrell, Z. Gross, J. R. Winkler and H. B. Gray, *J. Am. Chem. Soc.*, 2010, **132**, 9230.
- 19 (a) T. N. Singh-Rachford, A. Haefele, R. Ziesel and F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 16164.(b) T. Lazarides, S. Kuhri, G. Charalambidis, M. K. Panda, D. M. Guldi and A. G. Coutsolelos, *Inorg. Chem.*, 2012, **51**, 4193.
- 20 S. B. Piepho, P. N. Schatz, *Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism*; John Wiley and Sons: New York, 1983.