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Supporting Information

Novel Phosphorescent Cationic Iridium(III) Complexes with *o*-Carboranylation on the Ancillary N^N Ligand

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CONTENTS

I. General methods

In this paper, all the synthetic steps were carried out under an inert argon atmosphere using standard Schlenk and glovebox techniques unless otherwise noted. Commercial reagents were used without any further purification. All the solvents are freshly distilled, for example, THF and toluene were distilled on sodium / benzophenone as well as acetonitrile and EtOH on CaH_2. Dimeric $[(C^\wedge N)_2Ir(\mu{-}Cl)]_2$ complex was prepared by literature procedures.[S1] Intermediate compound $B_{10}H_{12}(Et_2S)_2$ was synthesized by a modified method according to literature reports.[S2,S3a] Compounds **1a−1j** [S3b] were synthesized according to literature. All NMR spectra (^{1}H−, ^{13}C−, and ^{11}B−) were obtained at ambient temperature on Bruker DRX−400 or Bruker DRX−500 spectrometer. Chemical shifts are reported relative to $CHCl_3$ / $CDCl_3$ (δ ^{1}H = 7.26 ppm, δ ^{13}C = 77.0 ppm) and external $Et_2O{\cdot}BF_3$ (δ ^{11}B = 0 ppm), respectively. Mass spectra were measured with a Bruker Daltonics Autoflex IITM MALDI−TOF MS spectrometer, Micromass GC−TOF for EI−MS (70 eV) and a ESI−MS (LCQ Fleet, Thermo Fisher Scientific). Phosphorescence measurements were carried out by using a Hitachi F−4600 fluorescence spectrophotometer. Electronic absorption spectra were recorded with Shimadzu UV−2550 spectrophotometers. Phosphorescence lifetimes were determined by an Edinburgh instrument laser impulse fluorometer with picosecond time resolution. Elemental analyses for C, H and N were performed on a Vario MICRO elemental analyzer. IR data were collected on a Bruker Vacuum FT−IR Spectrometer 80 V. X−ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the $\omega{-}2\theta$ scan mode.

II. X−ray structure determination

X−ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω−2θ scan mode. The data were corrected for Lorenz and polarization effects. Crystal structures were solved by direct methods and refined on F^2 by full−matrix least−squares methods using SHELXTL−2000. All calculations and molecular graphics were carried out using the SHELX−2000 program package and Mercury. CCDC 1535651 (**2a**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223−336−033; or deposit@ccdc.cam.ac.uk).

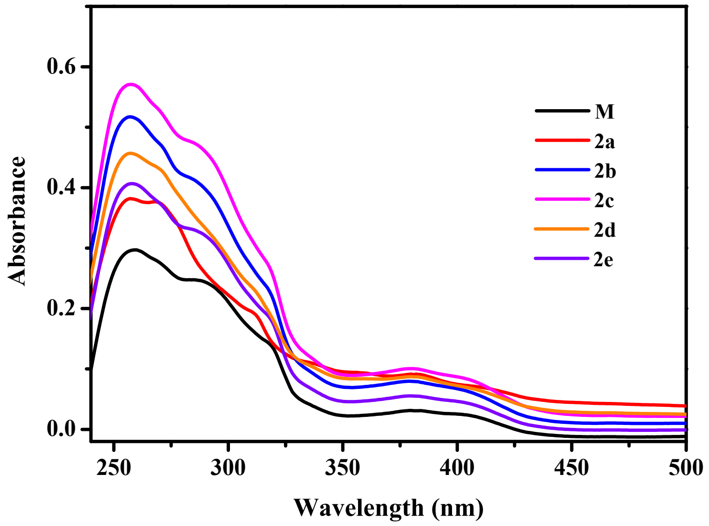
Table S1. Crystallographic Data for **2a**.

Compound	**2a**
chemical formula	$C_{34}H_{34}B_{10}N_4IrPF_6$
formula weight	943.95
crystal size (mm)	0.27 × 0.25 × 0.19
temperature (K)	291(2)
radiation(Å)	0.71073
crystal system	Triclinic
space group	P-1
a(Å)	13.659(9)
b(Å)	16.699(11)
c(Å)	19.574(12)
α(°)	84.627(11)
β(°)	74.209(10)
γ(°)	85.500(11)
V($Å^3$)	4271(5)
Z	4
ρ(calc) (g/cm^3)	1.466
F (000)	1844
absorp.coeff. (mm^{-1})	3.219
θ range (deg)	0.981–25.010
reflns collected	23057

indep. reflns	14776
Refns obs. [$I>2\sigma(I)$]	10404
GOF	1.076
R1/wR$_2$ [$I>2\sigma(I)$]	0.0913/0.1993
R1/wR$_2$ [all data]	0.0668/0.1904

III. Quantum yields determination

Absolute quantum yields of all the complexes in CH_2Cl_2 and in solid states were measured by employing an integrating sphere. Phosphorescence lifetime studies were performed with an Edinburgh FL 920 photo counting system with a hydrogen-filled lamp as the excitation source.



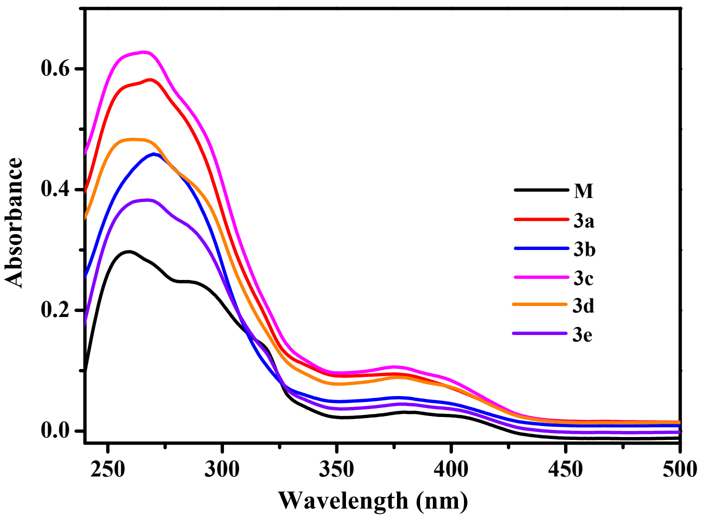


Figure S1. Absorption spectra: **Up**) complexes **2a**, **2b**, **2c**, **2d**, **2e**, and **Model**; **Down**) complexes **3a**, **3b**, **3c**, **3d**, **3e**, and **Model** in degassed CH_2Cl_2 at room temperature.

Table S2. Absorption of iridium(III) complexes in degassed CH_2Cl_2 solution at 298K.

Complexes	**$\lambda_{abs}{}^{a}$ [nm] (lgε)**
2a	257(2.4), 271(2.4), 310(3.7), 362(2.9)
2b	256(4.0), 282(3.8), 333(3.8), 379(3.1)
2c	256(4.0), 281(3.9), 318(3.9), 380(3.3)
2d	256(4.1), 295(3.9), 338(3.9), 383(3.3)
2e	258(4.1), 287(3.8), 334(3.8), 379(3.3)
M	258(4.0), 288(3.8), 319(3.8), 384(3.1)

3a	258(4.1), 269(3.8), 335(3.8), 379(3.4)
3b	269(4.1), 291(3.8), 335(3.7), 377(3.3)
3c	266(4.0), 285(3.8), 329(3.7), 375(3.3)
3d	269(4.2), 314(3.9), 340(3.8), 378(3.5)
3e	267(4.1), 289(3.8), 330(3.8), 381(3.4)

IV. Quantum chemical calculations

Geometries of the iridium(III) complexes were optimized by the density functional theory (DFT) method based on obtained crystal structures. The electronic transition energies including electron correlation effects were computed by the time dependent density functional theory (TD−DFT) method using B3LYP functional (TD−B3LYP). LANL2DZ basis set was used to treat the heavy metal iridium atom, whilst M06 functional with a basis set of 6−31G (d,p) for C, H, N, and B atoms. All calculations described here were performed by the Gaussian 09 program. Frequency calculations were also carriedout at the B3LYP/LANL2DZ/6−31G (d,p) level. All were found to be true minima based on no imaginary frequencies found.[S4]

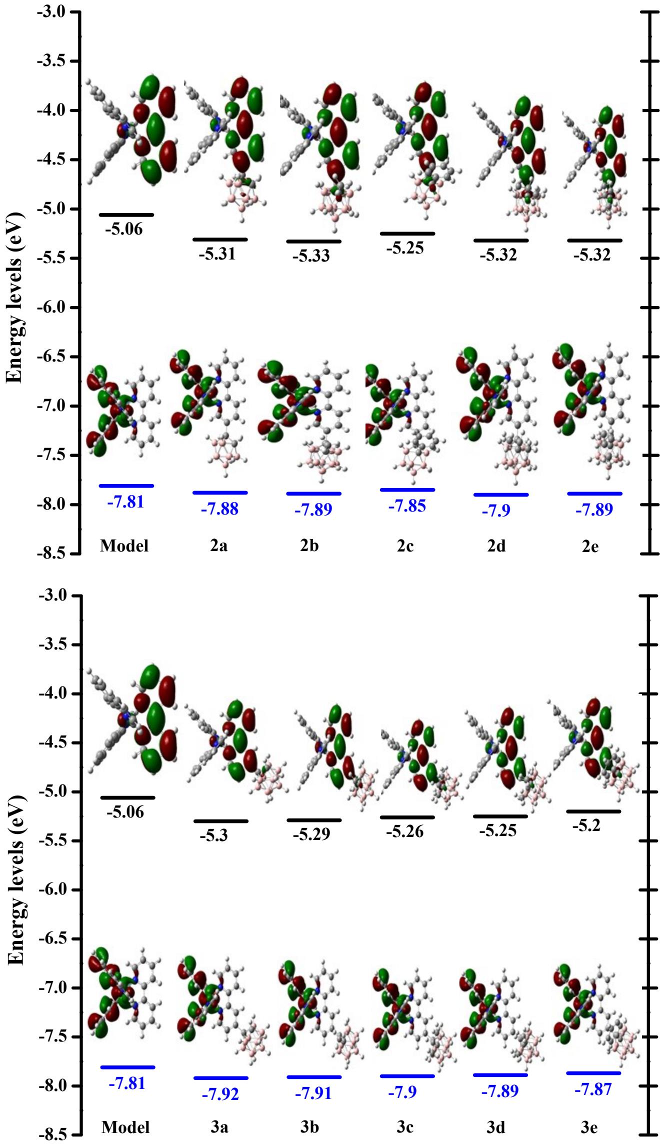


Figure S2. Calculated HOMO and LUMO of iridium(III) complexes in the ground state (S_0).

V. References

[S1]: S. Lamansky, P. Djurovich, D. Murphy, F. Abdel−Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304−4312.

[S2]: a) M. D. Marshall, R. M. Hunt, G. T. Hefferan, R. M. Adams and J. M. Makhlouf, *J. Am. Chem. Soc.* **1967**, *89*, 3361−3362; b) J. M. Makhlouf, W. V. Hough and G. T. Hefferan, *Inorg. Chem.* **1967**, *6*, 1196−1198; c) I. B. Sivaev, A. V. Prikaznov and D. Naoufal, *Collection. of Czechoslovak. Chem. Commun.* **2010**, *75*, 1149−1199; d) R. N. Grimes, *Carboranes*; 2nd ed., Vol.

9, Academic Press: New York, 2011, pp. 301–540; e) D. Power and T. R. Spalding, *Polyhedron* **1985**, *4*, 1329−1331; f) A. Toppino, A. R. Genady, M. E. El−Zaria, J. Reeve, F. Mostofian, J. Kent and J. F. Valliant, *Inorg. Chem.* **2013**, *52*, 8743−8749; g) L. A. Galliamova, M. V. Varaksin, O. N. Chupakhin, P. A. Slepukhin and V. N. Charushin, *Organometallics* **2015**, *34*, 5285−5290.

[S3]: a) X. Li, X. Tong, H. Yan, C. S. Lu, Q. Zhao, W. Huang, *Chem. Eur. J.* **2016**, *22*, 17282−17290; b) X. Li, X. Tong, Y. H. Yin, H. Yan, C. S. Lu, W. Huang, Q. Zhao, *Chem. Sci.* **2017**, DOI: 10.1039/C7SC00160F.

[S4]: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V.Bakken, C. Adamo, J. Jaram illo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.