



N-heterocyclic carbene platinum-butadiyne Click/iClick complexes. Towards blue-violet phosphorescence

Ru He^a, Jhonti Chakraborty^b, Tanjila Islam^a, Hadi D. Arman^a, Wendell P. Griffith^a,
Adam S. Veige^{b,*}, Kirk S. Schanze^{a,*}

^a Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas 78249, USA

^b Department of Chemistry, Center for Catalysis, University of Florida, Gainesville, FL 32611, USA

ARTICLE INFO

Article history:

Received 13 April 2022

Revised 24 June 2022

Accepted 29 June 2022

Available online 1 July 2022

Keywords:

Click reaction

iClick reaction

Phosphorescence

Platinum acetylide

N-heterocyclic carbene

ABSTRACT

By employing two different methods, namely, Click and iClick, a series of four *trans*-NHC-Pt(II) triazole-acetylide complexes containing benzyl (**3a**), methylnaphthalene (**3b**), methylantracene (**3c**), and phenyl (**3d**) substituents at the terminal triazole ring were synthesized and characterized. The traditional click approach involves first synthesizing a triazole-acetylene and then attaching to the Pt ion. In the iClick approach, the triazole is formed via cycloaddition by combining a *trans*-platinum butadiyne with the corresponding organic azide. The complexes were interrogated to determine the effects of conjugation and ligand substituent on their photophysical properties. Complex **3a** exhibits a photoluminescence lifetime of 4.3 μ s at 77 K. Ascribed to emission from conformers differing due to the torsion of the aryl acetylide ligands, employing different excitation wavelengths results in different emission spectra. Complex **3a** emits in the violet region with CIE coordinates of (0.159, 0.021) under 290 nm excitation and shifts to CIE coordinates of (0.161, 0.019) under 320 nm excitation. Complex **3d**, having a photoluminescence lifetime of 13.1 μ s at room temperature, emits in the sky-blue region with CIE coordinates of (0.237, 0.355).

© 2022 Elsevier B.V. All rights reserved.

1. Introduction

Organic light-emitting diodes (OLEDs) featuring low-cost fabrication and good power efficiency have emerged as one of the most promising candidates for future digital displays [1–4]. A driving force behind the extensive studies of OLEDs has been the introduction of electrophosphorescent devices based on phosphorescent metal complexes, which can harvest 100% of electrogenerated excitons [5–9]. Remarkable progress has already been achieved on iridium(III) complexes [5,7,9]. Square planar platinum(II) complexes have also been the focus of considerable research, which diversifies the efforts for OLEDs development [10–14]. The Commission International de L'Eclairage (CIE) coordinates of several Pt-complex based OLEDs approach the National Television System Committee (NTSC) coordinates for “pure” blue of (0.14, 0.08) [15–17]. Recent reports proved that the incorporation of NHC ligands into square planar *trans*-Pt(NHC)₂(CC-Ar)₂ complexes enable efficient phosphorescence originating from CC-Ar ligand centered ³ π,π^* states in the deep blue region [15,17–21]. Interestingly, the phosphorescence of *trans*-Pt(NHC)₂(CC-Ar)₂ complexes is easily tuned by modifying

the structure and extent of conjugation of the aryl acetylide ligands [15,19].

The concept of inorganic click (iClick), which was originally introduced to describe metal-azide/metal-acetylide cycloadditions [22–24], has been broadened to include the cycloaddition of either a metal-azide or metal-acetylide to their organic counterparts [25–30]. With the help of this powerful synthetic tool, complex metal-containing molecules and metalopolymers are easily synthesized in high yield [31–33]. In the past decade, iClick reactions within a metal coordination sphere [34–36] and the direct linking of two metal ions via iClick reactions have been successfully achieved [24,37–40]. For example, treatment of Pt-diazides with two equivalents of Au-acetylide enables the construction of a series of novel heterotrimetallic complexes [23].

In this work, we introduced triazole-acetylide-based ligands into a *trans*-Pt(NHC)₂(CC-Ar)₂ architecture via two different methods, namely, Click and iClick (Fig. 1). In the Click method, the triazole-acetylide ligands were first prepared from 1,3-butadiynyltrimethylsilane and the corresponding azide, then the as-obtained triazole-acetylide ligands were attached to the Pt(II) center. The iClick pathway involved the cycloaddition between the butadiyne functionality bound to Pt(II) and the corresponding organic azide. The as-obtained **3a** compound displays near-UV/violet phosphorescence at 77 K, and **3d** exhibits sky-blue emission at

* Corresponding authors.

E-mail addresses: veige@chem.ufl.edu (A.S. Veige), kirk.schanze@utsa.edu (K.S. Schanze).

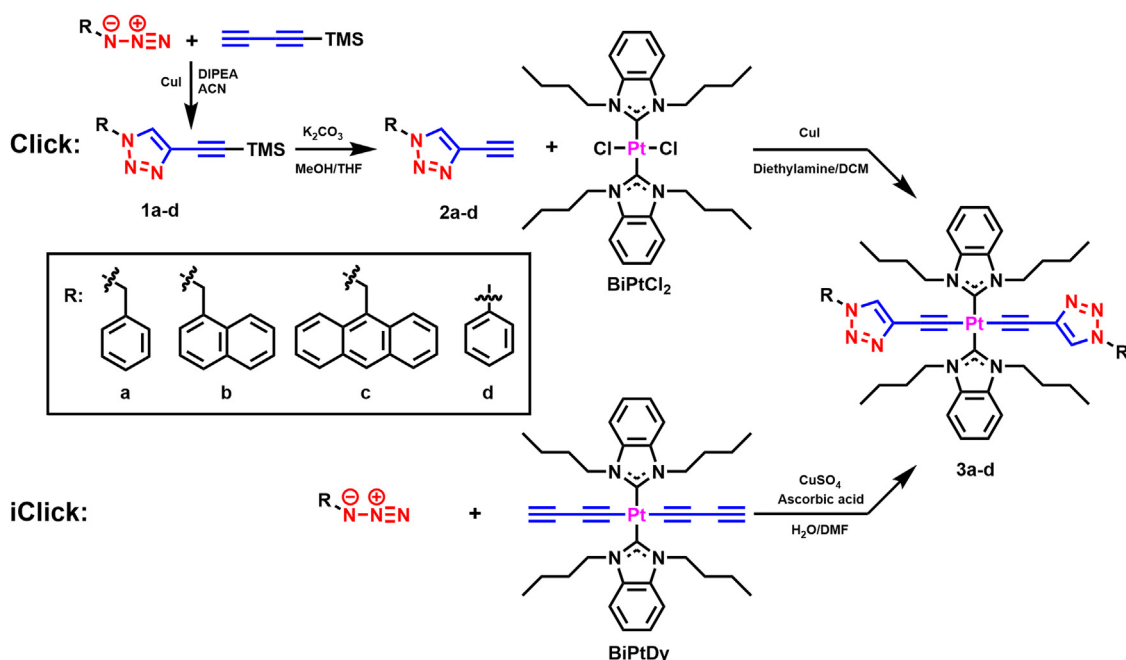


Fig. 1. Synthetic schemes for Click and iClick methods.

room temperature. This work expands the design possibility of the *trans*-Pt(NHC)₂(CC-Ar)₂ platform and provides new concepts for blue-violet phosphorescent materials development.

In an example of the Click method, 1-benzyl-4-ethynyl-1H-1,2,3-triazole (**2a**) was first synthesized via the Cu-catalyzed organic click reaction between benzyl azide and freshly prepared 1,3-butadiynyltrimethylsilane, followed by the removal of the trimethylsilyl protecting group. Treatment of **BiPtCl₂** with 2.5 equivalents of **2a** in HNEt₂/dichloromethane (DCM) with CuI as the catalyst at room temperature provides **3a** as a pale-yellow crystalline solid in 33% isolated yield via flash column chromatography with DCM/ethyl acetate as the eluent. In the iClick pathway, combining air-stable **BiPtDy** with two equivalents of benzyl azide initiates a copper-catalyzed double iClick on the terminal triple bonds of each butadiyne ligand on the platinum center. An aqueous solution of CuSO₄ and ascorbic acid generates Cu(I) *in-situ*. Diffusion of pentane into a DCM solution of the crude product gives compound **3a** as colorless crystals, in 55% isolated yield. Evidence of purity and identity of **3a** synthesized by both methods comes from ¹H NMR spectroscopy (Fig. 2). A resonance for the -CH₂- protons attached to the nitrogen of the NHC ligands appears at 4.76 ppm as a triplet, confirming the *trans* configuration [41]. The singlet at 5.31 ppm for the -CH₂- protons of the benzylic carbon and the distinct singlet at ~7 ppm, which can be assigned to the -CH proton of the triazole ring, further confirm the success of the iClick reaction.

By employing phenyl azide in both the Click and iClick methods, *trans*-NHC Pt(II) triazole-acetylide complex **3d** was also successfully obtained. In complex **3d** there is direct conjugation between the triazole and phenyl units, and this is expected to influence the optical properties of the complex (*vide infra*). In the Click pathway, 4-ethynyl-1-phenyl-1H-1,2,3-triazole (**2d**), which was synthesized via the same procedure as the synthesis of **2a**, was attached to **BiPtCl₂** to give **3d** as a white solid with a yield of 37%. In contrast, a double-iClick reaction of phenyl azide (2 eq) with **BiPtDy** (1 eq) also affords **3d** in 53% yield. ¹H NMR spectra of **3d** prepared by both methods are depicted in Fig. 2. The NMR peak intensities are relatively low due to the poor solubility of **3d**

in CDCl₃ and CD₂Cl₂. The single triplet between 4.75 and 5.00 ppm confirms the *trans* configuration of **3d**. The success of the double-iClick reaction was validated by the complete disappearance of the resonances at 1.49 ppm for the terminal -CH protons of **BiPtDy** and the appearance of the distinct singlet at 7.52 ppm, which is assigned to the proton of the triazole ring.

To extend the substrate scope, we further employed 1-(azidomethyl)naphthalene and 9-(azidomethyl)anthracene featuring fluorescent chromophores in Click and iClick methods. With 1-(azidomethyl)naphthalene as the starting material, we were able to obtain compound **3b** with a good yield via both Click and iClick methods (55% in both pathways). In contrast, compound **3c** was only successfully synthesized via the Click pathway. **BiPtDy** appears to be inert to 9-(azidomethyl)anthracene in the iClick method, possibly due to unfavorable steric interactions between the **BiPtDy** and the 9-(azidomethyl) anthracene. In most cases, the overall isolated yields from the iClick reactions are greater than the Click approach. However, there appear to be steric interactions that limit the synthesis of **3c** by the iClick method, suggesting that this method may be more limited by unfavorable steric interactions on the reaction pathway [33].

The structures and geometries of **3a**, **3b**, **3c**, and **3d** were further confirmed by single-crystal X-ray crystallography. The crystal structures of **3a**, **3c** and **3d** are shown in Fig. 3, and the crystal structure of **3b** is shown in the Supporting Information. Detailed crystallographic data are reported in the Supporting Information. X-ray crystallography confirms the *trans* configuration of the Pt(II)(NHC)₂(CC-Ar)₂ center in all four complexes with the Pt atom residing in an inversion center. Complex **3a** features a Pt-C_{carbene} bond length of 2.021(2) Å and a Pt-C_{acetylide} bond length of 1.997(3) Å. The Pt-C_{carbene} and Pt-C_{acetylide} bond lengths of **3d** are 2.029(4) Å and 2.008(5) Å, respectively. These bond lengths are similar to those of previously reported Pt-NHC complexes [15,18–20]. For **3a**, the dihedral angle between the NHC plane and the PtC₄ plane (defined by C_{carbene}-Pt-C_{acetylide}) is 86.8(1)°, the dihedral angle between the triazole ring and PtC₄ plane is 46.9(1)°. While for **3d**, the dihedral angle between the NHC plane and PtC₄ is 88.7(3)°. In this case, the triazole ring is almost perpendicular to

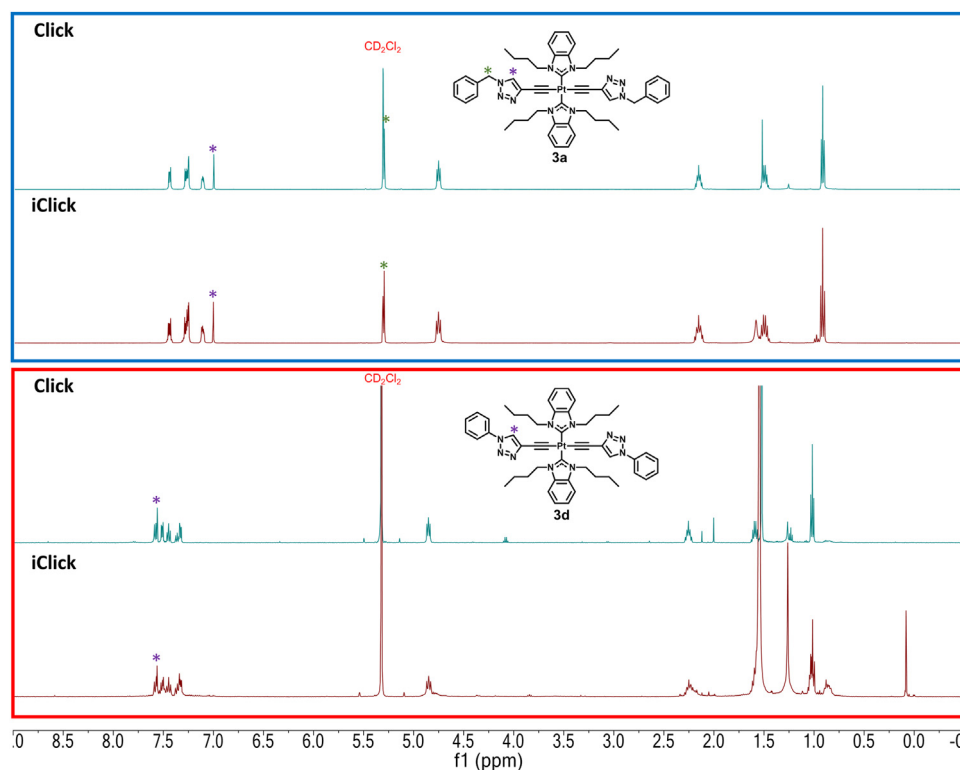


Fig. 2. ^1H NMR spectra of **3a** and **3d** synthesized via **Click** and **iClick** methods.

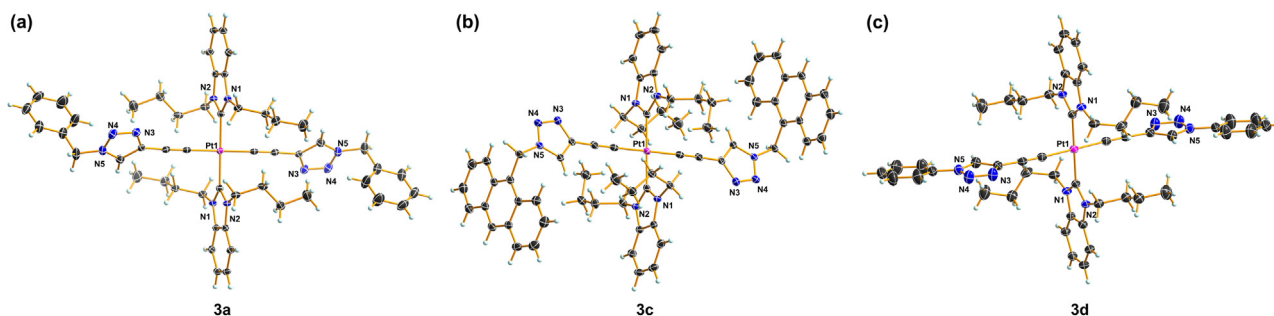


Fig. 3. Crystal structures of **3a**, **3c** and **3d**, with ellipsoids shown at the 50% probability level. Carbon atoms are shown in gray, and hydrogen atoms are shown in light turquoise; all are unlabeled.

the PtC_4 plane with a dihedral angle of $88.1(2)^\circ$. Furthermore, the phenyl ring and the triazole ring of the acetylide ligand of **3d** are almost coplanar with a small dihedral angle of $6.7(2)^\circ$. The structural features of **3c** are generally similar to **3a**, with the notable exception that the dihedral angle between the triazole ring and PtC_4 plane in **3c** is $14.6(1)^\circ$ which is substantially less than in **3a**. This difference could arise from crystal packing effects arising from the bulky anthracene substituents.

To probe the effect of the conjugation in the triazole-acetylide ligands and the arylene substituents on the photoluminescence of $\text{trans-Pt}(\text{NHC})_2(\text{triazole-acetylide})_2$ complexes, photophysical studies were executed for **3a**–**3d**. Data for **3a** and **3d** are included in the text below, while selected data for **3b** and **3c** are provided in the supporting information (Fig. S36, Table S2). We note that the photophysical properties of **3b** and **3c** were limited to measurements in room temperature dichloromethane (DCM) solution, since these complexes are not soluble in other common spectroscopic solvents, including tetrahydrofuran and 2-methyltetrahydrofuran (THF and 2-MTHF, respectively). (The latter solvent is required for low temperature measurements.)

First, the UV–visible absorption spectra of **3a** and **3d** were measured in THF solution at room temperature (Fig. 4). Complex **3a** features absorption below 330 nm with a maximum at 290 nm and a shoulder at 270 nm. A similar absorption maximum, 291 nm, was observed for **3d**. However, **3d** displays an additional shoulder band at lower energy at 315 nm, apparently due to the extended conjugation of the phenyl-triazole-acetylide ligands.

Complex **3a** features only very weak photoluminescence ($\phi_{\text{em}} < 0.01$) at room temperature. As shown in Fig. S35, the emission for the air-saturated sample appears as a weak fluorescence with $\lambda_{\text{max}} \sim 350$ nm; weak phosphorescence is seen in the degassed sample at room temperature which appears as a shoulder peak at 375 nm. In contrast, in 2-MTHF glass matrix at 77 K, **3a** features a prominent phosphorescence in the near-UV region (Fig. 4). The decay lifetime of the emission of **3a** is $4.0 \mu\text{s}$ at 77 K, consistent with assignment to phosphorescence. Interestingly, under different excitation wavelengths (290 and 320 nm) at 77 K, two sets of emission onsets are observed, which can be assigned to the non-equilibrating conformers of **3a** with different emission energy that is hypothesized to arise due to torsion of the aryl acetylide ligands.

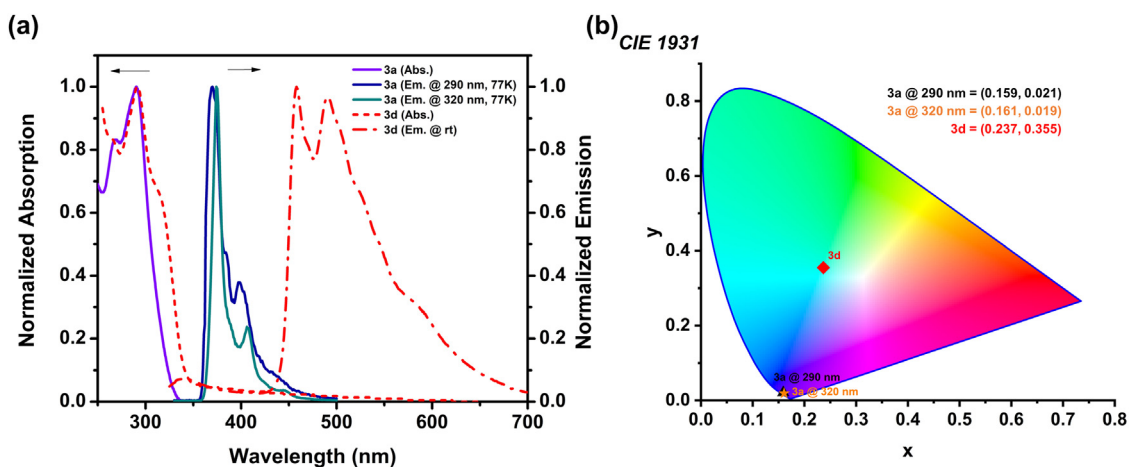


Fig. 4. Overlaid UV-visible absorption and photoluminescence of **3a** and **3d**. The absorption of **3a** and **3d** were recorded in THF at room temperature. Emission spectra of **3a** were measured in 2-MTHF at 77 K under 290 nm and 320 nm excitation. The emission spectrum of **3d** was measured at room temperature in N_2 degassed THF solution with 300 nm excitation. The spectrum of **3d** in 2-MTHF at 77 K is provided in the Supporting Information.

Under 290 nm excitation, **3a** displays a violet emission with a maximum of 370 nm and CIE coordinates of (0.159, 0.021). The emission maximum of **3a** red-shifted to 374 nm with CIE coordinates of (0.161, 0.019) under 320 nm excitation. Similar excitation wavelength dependent emission spectra have been observed in related *trans*-Pt(PR₃)₂(CC-Ar)₂ and *trans*-Pt(NHC)₂(CC-Ar)₂ complexes, and density functional theory (DFT) calculations support the premise that the energy of the phosphorescent triplet state varies with torsion of the aryl ring around the -CC- bond axis [15,20,42,43].

Interestingly, the emission properties of **3d** are substantially different compared to **3a**. As noted below, these differences likely arise due to the enhanced π -conjugation that occurs because in **3d** the phenyl is directly conjugated with the triazole ring. In particular, **3d** displays photoluminescence at room temperature ($\phi_{em} = 0.021$) in degassed THF solution (Fig. 4) and the emission lifetime is 14.5 μ s at room temperature. The photoluminescence of **3d** at room temperature features a maximum at 458 nm and a vibronic sideband at 490 nm (CIE coordinates of (0.237, 0.355)). The emission band of **3d** is broadened compared to **3a**, possibly due to the mixing of lower frequency vibrational modes involving torsion of the phenyl group. Due to low solubility of **3d** in 2-MTHF it is difficult to study its photophysics at low temperature; however, we were able to obtain an emission spectrum for the complex at 77 K and it is similar to that observed at room temperature (see Fig. S37).

It is evident that for both **3a** and **3d** the emission that is observed originates from a mainly triazole ligand centered $^3\pi, \pi^*$ state [15,17–20]. As noted previously, the emission from **3d** occurs at considerably lower energy (longer wavelength) compared to **3a**. The difference in emission energies is due to the difference in conjugation in the triazole ligands. For **3a** the conjugation comprises only the acetylide unit and triazole ring, whereas in **3d** the conjugation extends into the phenyl unit. This difference clearly gives rise to a stabilization of the intraligand $^3\pi, \pi^*$ state. In addition, the difference in emission energy of **3a** and **3d** can be used to explain the fact that the former is virtually non-emissive at room temperature. In particular, in previous work we have shown that for *trans*-Pt(NHC)₂(CC-Ar)₂ complexes, the room temperature emission quantum yield decreases sharply for complexes that have phosphorescence at $\lambda < 450$ nm [42]. This is due to thermally-activated crossing to one or more metal centered d-d states that provide a path for rapid non-radiative decay [42]. Finally, it is noteworthy that the emission lifetime of **3d** at room temperature is longer than **3a** at 77 K. This difference suggests

that the non-radiative (and possibly the radiative) decay rate(s) in **3d** is (are) substantially lower. One possible reason to explain this is that spin-orbit coupling is lower in **3d** due to the conjugation of the phenyl group with the triazole ring weakening the metal-ligand electronic interaction. Lower spin-orbit coupling would decrease the rates of radiative and non-radiative decay of the phosphorescent intraligand $^3\pi, \pi^*$ state.

The absorption and emission of the naphthalene (**3b**) and anthracene (**3c**) substituted complexes taken in degassed dichloromethane (DCM) solution at room temperature are shown in the supporting information (Fig. S36). The absorption spectra are similar to **3a**, with a strong band at 290 nm in the UV. The anthracene complex **3c** features an additional absorption feature band in the near UV (330–390 nm) that can be ascribed to the anthracene chromophores. The emission from both **3b** and **3c** is dominated by the appended arylene chromophores. For the naphthyl substituted complex **3b** fluorescence with $\lambda_{max} \sim 330$ nm ($\phi_{em} = 0.04$, $\tau = 960$ ps) and weak phosphorescence with $\lambda_{max} \sim 540$ nm is observed. The anthracene complex **3c** only exhibits fluorescence characteristic of the anthracene chromophore with a vibronic structured emission with $\lambda_{max} \sim 417$ nm ($\phi_{em} = 0.024$, $\tau = 1030$ ps).

2. Conclusion

A set of four novel complexes of the type *trans*-Pt(NHC)₂(CC-Ar)₂ have been synthesized and characterized, where Ar is a 1,2,3-triazole moiety. The complexes have been prepared by two distinct synthetic pathways, one involving the coupling reaction between the *trans*-Pt(NHC)₂Cl₂ precursor and the acetylene-substituted triazole. The second approach involved the novel iClick reaction between the organic azide and the 1,3-butadiyne complex, Pt(NHC)₂(CC-CC-H)₂. The X-ray crystal structures of the four novel complexes are reported and their geometries are similar to previously reported *trans*-Pt(NHC)₂(CC-Ar)₂ complexes. Absorption and emission studies reveal that benzyl-substituted complex **3a** exhibits strong phosphorescence in the near-UV region. By contrast, complex **3d**, which features a phenyl substituent that is conjugated with the 1,2,3-triazole ring, exhibits phosphorescence in the blue region. The substantial red-shift is attributed to increase delocalization of the chromophore involved in the triplet state due to the conjugation between the triazole and phenyl rings. This work points the way towards the design and synthesis of phosphors that

emit in the near-UV region, with potential for application in blue-violet phosphorescent organic light emitting diodes.

3. Experimental section

3.1. Synthesis

Synthesis, characterization, and X-ray structural data are included in the Supporting Information.

3.2. Photophysical properties

UV-vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Steady-state emissions in THF at room temperature and in 2-MTHF at 77 K were measured on an Edinburgh FLS-1000 photoluminescence spectrometer. The solutions were prepared using deaerated THF in the glovebox. Emission quantum yields were determined with an integrating sphere attachment for the FLS-1000 spectrometer and using accompanying software. The low-temperature emission was measured using a special designed cuvette equipped with a Dewar flask. Emission lifetimes for **3a** (at 77 K) and **3b** and **3c** were obtained on a PicoQuant FluoTime 300 time-correlated single-photon counting (TCSPC) spectrophotometer using the Taiko pulsed LED source ($\lambda = 313$ nm). Phosphorescence lifetime measurement of **3d** was carried out using an Edinburgh LP920 spectrophotometer (Edinburgh Instruments) and a Continuum Surelite II series Nd:YAG laser (third harmonic $\lambda = 355$ nm, 4 mJ per pulse) as the excitation source.

Declaration of Competing Interest

None

Acknowledgment

Work at the University of Texas at San Antonio, which focused on the organic click synthesis and photophysical characterization of the complexes, was supported by the [National Science Foundation](#) (Grant No. [CHE-1904288](#), KSS). Work at the University of Florida, focused on the iClick synthesis pathway, was supported by the [US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering](#) under award [DE-SC0020008](#) (ASV and KSS). X-ray crystallography was carried out at the University of Texas at San Antonio on a diffractometer obtained with support from the [National Science Foundation](#) (Grant [MRI 1920057](#)). High resolution mass spectroscopy was carried out on an instrument obtained with support from the [National Science Foundation](#) (Grant [MRI 2117691](#)).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jorgchem.2022.122440](#).

References

- [1] B. Geffroy, P. Le Roy, C. Prat, Organic light-emitting diode (OLED) technology: materials, devices and display technologies, *Polymer International* 55 (2006) 572–582.
- [2] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, Stretchable active-matrix organic light-emitting diode display using printable elastic conductors, *Nature Materials* 8 (2009) 494–499.
- [3] J.W. Sun, J.H. Lee, C.K. Moon, K.H. Kim, H. Shin, J.J. Kim, A fluorescent organic light-emitting diode with 30% external quantum efficiency, *Advanced Materials* 26 (2014) 5684–5688.
- [4] N.T. Kalyani, S. Dhoble, Organic light emitting diodes: Energy saving lighting technology—A review, *Renewable and Sustainable Energy Reviews* 16 (2012) 2696–2723.
- [5] J. Lee, H.-F. Chen, T. Batagoda, C. Coburn, P.I. Djurovich, M.E. Thompson, S.R. Forrest, Deep blue phosphorescent organic light-emitting diodes with very high brightness and efficiency, *Nature Materials* 15 (2016) 92–98.
- [6] M. Baldo, M. Thompson, S. Forrest, Phosphorescent materials for application to organic light emitting devices, *Pure and Applied Chemistry* 71 (1999) 2095–2106.
- [7] C. Adachi, M.A. Baldo, M.E. Thompson, S.R. Forrest, Nearly 100% internal phosphorescence efficiency in an organic light-emitting device, *Journal of Applied Physics* 90 (2001) 5048–5051.
- [8] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Highly efficient phosphorescent emission from organic electroluminescent devices, *Nature* 395 (1998) 151–154.
- [9] M. Baldo, S. Lamansky, P. Burrows, M. Thompson, S. Forrest, Very high-efficiency green organic light-emitting devices based on electrophosphorescence, *Applied Physics Letters* 75 (1999) 4–6.
- [10] R.C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S.R. Forrest, M.E. Thompson, Efficient, saturated red organic light emitting devices based on phosphorescent platinum (II) porphyrins, *Chem. Mater.* 11 (1999) 3709–3713.
- [11] C.M. Che, C.C. Kwok, S.W. Lai, A.F. Rausch, W.J. Finkenzeller, N. Zhu, H. Yersin, Photophysical properties and OLED applications of phosphorescent platinum (II) Schiff base complexes, *Chemistry—A European Journal* 16 (2010) 233–247.
- [12] J. Kalinowski, V. Fattori, M. Cocchi, J.G. Williams, Light-emitting devices based on organometallic platinum complexes as emitters, *Coord. Chem. Rev.* 255 (2011) 2401–2425.
- [13] X.C. Hang, T. Fleetham, E. Turner, J. Brooks, J. Li, Highly efficient Blue-Emitting cyclometalated platinum (II) complexes by judicious molecular design, *Angewandte Chemie* 125 (2013) 6885–6888.
- [14] T. Fleetham, G. Li, J. Li, Phosphorescent Pt (II) and Pd (II) complexes for efficient, high-color-quality, and stable OLEDs, *Advanced Materials* 29 (2017) 1601861.
- [15] R. He, Z. Xu, S. Valandro, H.D. Arman, J. Xue, K.S. Schanze, High-Purity and Saturated Deep-Blue Luminescence from trans-NHC Platinum (II) Butadiyne Complexes: Properties and Organic Light Emitting Diode Application, *ACS Appl. Mater. Interfaces* 13 (2021) 5327–5337.
- [16] T. Fleetham, G. Li, L. Wen, J. Li, Efficient “pure” blue OLEDs employing tetradentate Pt complexes with a narrow spectral bandwidth, *Advanced Materials* 26 (2014) 7116–7121.
- [17] J.D. Bullock, Z. Xu, S. Valandro, M. Younus, J. Xue, K.S. Schanze, Trans-N-(Heterocyclic carbene) platinum (II) acetylide chromophores as phosphors for OLED applications, *ACS Appl. Electron. Mater.* 2 (2020) 1026–1034.
- [18] J.D. Bullock, A. Salehi, C.J. Zeman IV, K.A. Abboud, F. So, K.S. Schanze, Search of Deeper Blues: Trans-N-Heterocyclic Carbene Platinum Phenylacetylide as a Dopant for Phosphorescent OLEDs, *ACS Appl. Mater. Interfaces* 9 (2017) 41111–41114.
- [19] R.W. Winkel, G.G. Dubinina, K.A. Abboud, K.S. Schanze, Photophysical properties of trans-platinum acetylide complexes featuring N-heterocyclic carbene ligands, *Dalton Transactions* 43 (2014) 17712–17720.
- [20] S.R. Valandro, R. He, J.D. Bullock, H. Arman, K.S. Schanze, Ultrafast Excited-State Dynamics in trans-(N-Heterocyclic carbene) platinum (II) Acetylide Complexes, *Inorganic Chemistry* (2021).
- [21] R. He, R.A. Domingues, S. Valandro, K.S. Schanze, Platinum Poly-yne Featuring N-Heterocyclic Carbene Ligands: Synthesis, Properties, and Organic Light-Emitting Diode Application, *Macromolecules* 54 (2021) 9888–9895.
- [22] X. Yang, S. Wang, I. Ghiviriga, K.A. Abboud, A.S. Veige, Organogold oligomers: exploiting iClick and aurophilic cluster formation to prepare solution stable Au 4 repeating units, *Dalton Transactions* 44 (2015) 11437–11443.
- [23] A.R. Powers, X. Yang, T.J. Del Castillo, I. Ghiviriga, K.A. Abboud, A.S. Veige, Inorganic click (iClick) synthesis of heterotrimeric Pt II/Au I 2 complexes, *Dalton Transactions* 42 (2013) 14963–14966.
- [24] T.J. Del Castillo, S. Sarkar, K.A. Abboud, A.S. Veige, 1, 3-Dipolar cycloaddition between a metal-azide (Ph₃PAuN₃) and a metal-acetylide (Ph₃PAuCCPh): An inorganic version of a click reaction, *Dalton Transactions* 40 (2011) 8140.
- [25] T. Cruchter, K. Harms, E. Meggers, Strain-promoted azide-alkyne cycloaddition with ruthenium (II)-azido complexes, *Chem.-Eur. J.* 19 (2013) 16682–16689.
- [26] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, Diiron and diruthenium aminocarbene complexes containing pseudohalides: stereochemistry and reactivity, *Inorg. Chim. Acta* 358 (2005) 1204–1216.
- [27] C.-W. Chang, G.-H. Lee, Synthesis of ruthenium triazoloto and tetrazoloto complexes by 1, 3-dipolar cycloadditions of ruthenium azido complex with alkynes and alkenes and regioselective alkylation of triazolates, *Organometallics* 22 (2003) 3107–3116.
- [28] S. Miguel-Fernández, S. Martínez de Salinas, J. Díez, M. Gamasa, E. Lastra, 1, 3-Dipolar cycloadditions of ruthenium (II) azido complexes with alkynes and nitriles, *Inorganic Chemistry* 52 (2013) 4293–4302.
- [29] D.V. Partyka, J.B. Updegraff, M. Zeller, A.D. Hunter, T.G. Gray, Carbon–gold bond formation through [3+ 2] cycloaddition reactions of gold (I) azides and terminal alkynes, *Organometallics* 26 (2007) 183–186.
- [30] X. Yang, S. VenkatRamani, C.C. Beto, T.J. Del Castillo, I. Ghiviriga, K.A. Abboud, A.S. Veige, Single versus double Cu (I) catalyzed [3+ 2] azide/platinum diacetylide cycloaddition reactions, *Organometallics* 36 (2017) 1352–1357.
- [31] C. Beto, E. Holt, Y. Yang, I. Ghiviriga, K. Schanze, A. Veige, A new synthetic route to in-chain metallopolymers via copper (I) catalyzed azide-platinum-acetylide iClick, *Chem. Commun.* 53 (2017) 9934–9937.

- [32] C.C. Beto, Y. Yang, C.J. Zeman IV, I. Ghiviriga, K.S. Schanze, A.S. Veige, Cu-catalyzed azide-Pt-acetylide cycloaddition: Progress toward a conjugated metallopolymer via iClick, *Organometallics* 37 (2018) 4545–4550.
- [33] Y.-H. Shen, A.M. Esper, I. Ghiviriga, K.A. Abboud, K.S. Schanze, C. Ehm, A.S. Veige, SPAAC iClick: progress towards a bioorthogonal reaction incorporating metal ions, *Dalton Transactions* 50 (2021) 12681–12691.
- [34] M.C. Clough, P.D. Zeits, N. Bhuvanesh, J.A. Gladysz, Toward permatalated alkyne/azide 3+ 2 or “click” cycloadducts, *Organometallics* 31 (2012) 5231–5234.
- [35] L. Casarrubios, M.C. de la Torre, M.A. Sierra, The “Click” reaction involving metal azides, metal alkynes, or both: An exploration into multimetal structures, *Chemistry–A European Journal* 19 (2013) 3534–3541.
- [36] K.S. Singh, V. Svitlyk, Y. Mozharivskyj, Mono and dinuclear areneruthenium (II) triazoles by 1, 3-dipolar cycloadditions to a coordinated azide in ruthenium (II) compounds, *Dalton Transactions* 40 (2011) 1020–1023.
- [37] C.C. Beto, C.J. Zeman IV, Y. Yang, J.D. Bullock, E.D. Holt, A.Q. Kane, T.A. Makal, X. Yang, I. Ghiviriga, K.S. Schanze, An application exploiting aurophilic bonding and iClick to produce white light emitting materials, *Inorganic Chemistry* 59 (2020) 1893–1904.
- [38] A.R. Powers, I. Ghiviriga, K.A. Abboud, A.S. Veige, Au-iClick mirrors the mechanism of copper catalyzed azide-alkyne cycloaddition (CuAAC), *Dalton Transactions* 44 (2015) 14747–14752.
- [39] C.C. Beto, X. Yang, A.R. Powers, I. Ghiviriga, K.A. Abboud, A.S. Veige, Expanding iClick to group 9 metals, *Polyhedron* 108 (2016) 87–92.
- [40] C.J. Zeman IV, Y.-H. Shen, J.K. Heller, K.A. Abboud, K.S. Schanze, A.S. Veige, Excited-State Turn-On of Aurophilicity and Tunability of Relativistic Effects in a Series of Digold Triazolates Synthesized via iClick, *J. Am. Chem. Soc.* 142 (2020) 8331–8341.
- [41] Y. Zhang, O. Blacque, K. Venkatesan, Highly Efficient Deep-Blue Emitters Based on cis and trans N-Heterocyclic Carbene Pt(II) Acetylide Complexes: Synthesis, Photophysical Properties, and Mechanistic Studies, *Chemistry–A European Journal* 19 (2013) 15689–15701.
- [42] J.D. Bullock, S.R. Valandro, A.N. Sulicz, C.J. Zeman IV, K.A. Abboud, K.S. Schanze, Blue Phosphorescent trans-N-Heterocyclic Carbene Platinum Acetylides: Dependence on Energy Gap and Conformation, *J. Phys. Chem. A* 123 (2019) 9069–9078.
- [43] K. Glusac, M.E. Köse, H. Jiang, K.S. Schanze, Triplet Excited State in Platinum–Acetylide Oligomers: Triplet Localization and Effects of Conformation, *J. Phys. Chem. B* 111 (2007) 929–940.