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Tunable Visible Light Emission of Self-Assembled Rhomboidal Metallacycles

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Supporting Information

ABSTRACT: Supramolecular coordination complexes (SCCs) have been proposed for applications necessitating photon emitting properties; however, two critical characteristics, facile tunability and high emission quantum yields, have yet to be demonstrated on SCC platforms. Herein, a series of functionalized D_{2h} [D_2A_2] rhomboids (D = 2,6-bis(4-ethynylpyridine)aniline-based ligands; A = 2,9-bis[*trans*-Pt(PEt_3)$_2$$NO_3$]phenanthrene) is described with emission wavelengths spanning the visible region (λ_{max} = 476−581 nm). Tuning was achieved by simple functional group modifications *para* to the aniline amine on the donor building block. Steady-state absorption and emission profiles were obtained for each system and are discussed. When the Hammett σ_{para} constants for the functional groups *para* to the aniline amine were plotted versus the wavenumber (cm^{-1}) for the λ_{max} of the emission profile, a linear relationship was observed. By utilizing this relationship, the emission wavelength of a given rhomboid can be predetermined on the basis of the Hammett constant of the functionality employed on the donor precursor. This range of visible light emission for a suite of simple rhomboids along with the predictive nature of the wavelength of emission is unprecedented for these types of systems.

The ability to tune the emission of materials in a simple fashion is of great interest in the manufacturing of photovoltaics,[1] light-emitting diodes,[2] nonlinear optical (NLO) materials,[3] bio-imaging agents,[4] and other photon emitting devices, motivating efforts to develop novel systems that are readily tunable, particularly in the visible region. The synthesis of tunable transition-metal-based molecular organic frameworks (MOFs) has seen intense growth over the past several years, with tunability afforded by various methods: (i) incorporation of fluorescent ligands or luminescent metal nodes in the core structure, (ii) alteration of the shape and size of the framework, (iii) guest inclusion, or (iv) external stimulus.[5] Unfortunately, MOFs are prone to morphological changes when external sources or stimuli are used to facilitate luminescence and are fraught with solubility issues.[6] Supramolecular coordination complexes (SCCs) preserve the attractive features of MOFs, such as facile building block modularity, yet also afford increased solubilities and lend themselves to small-molecule characterization techniques owing to their discrete nature.[7] Reports of both MOF and SCC systems that display tunable wavelengths spanning the visible spectrum have largely been dominated by lanthanide-based systems or metal−organic structures that contain lanthanide cations as guests, and only recently have lanthanide-free systems received attention.[5b,8]

The attractive photophysical properties of mono- and multinuclear bis(phosphine) Pt(II) metal complexes (i.e., tunability, low-energy and long-lived excited states)[9] have prompted their incorporation into SCCs, wherein these characteristics can be exploited in large metallacycles. In particular, we have developed highly emissive rhomboids based on aniline-containing donors and Pt-based metal acceptors.[10] Having established the chemistry of visibly emitting rhomboids with high quantum yields, we sought to achieve the second, hitherto unrealized, goal of tunable emission.

Herein, we report the synthesis of a series of D_{2h} [D_2A_2] rhomboidal complexes, **7**−**11** (D = 2,6-bis(4-ethynylpyridine)-aniline-based ligands, **1**−**5**; A = 2,9-bis[*trans*-Pt(PEt_3)$_2$$NO_3$]-phenanthrene, **6**), which differ only by the pendant functional group *para* to the aniline core and display tunable wavelengths spanning the visible spectrum. Moreover, when the wavenumber (cm^{-1}) of the λ_{max} of emission profiles for each rhomboid is plotted versus the Hammett σ_{para} constant for the pendant functional groups, a linear relationship is obtained. The steady-state absorption and emission profiles were collected for each rhomboidal complex and precursor ligand and are discussed.

Ligand **1** was prepared via a Sonogashira reaction with 2,6-diiodo-4-nitroaniline and 4-ethynylpyridine hydrochloride; ligands **2** and **4** were prepared in a similar manner, while **5** was synthesized by reducing the nitro group in **1** (Supporting Information). After being stirred 24 h, a solution containing a 1:1 stoichiometric mixture of ligand **1**, **2**, **3**, **4**, or **5**, respectively, with **6** affords D_{2h} [D_2A_2] endohedral amine exo-functionalized rhomboids **7**−**11** in quantitative yields (Scheme 1).

SCCs **7**−**11** have a high-energy band centered at 305−318 nm (Figure 1, top; Table 1) that increases in wavelength with the electron-donating ability of the pendant functionality. This band was previously investigated for **9** and reported to be intimately related to the ethynyl group in ligand **3**.[10g] It was determined, unlike the low-energy band, that the molar absorption coefficient of this band is relatively unaffected by the nature of the functional group *para* to the aniline amine.[10g] SCC **7** has a high-energy band maximum of 305 nm and a molar absorption coefficient of 114 000 cm^{-1} M^{-1}, while **11** has a high-energy band maximum of 317 nm and a molar absorption coefficient of 97 500 cm^{-1} M^{-1}. The low-energy

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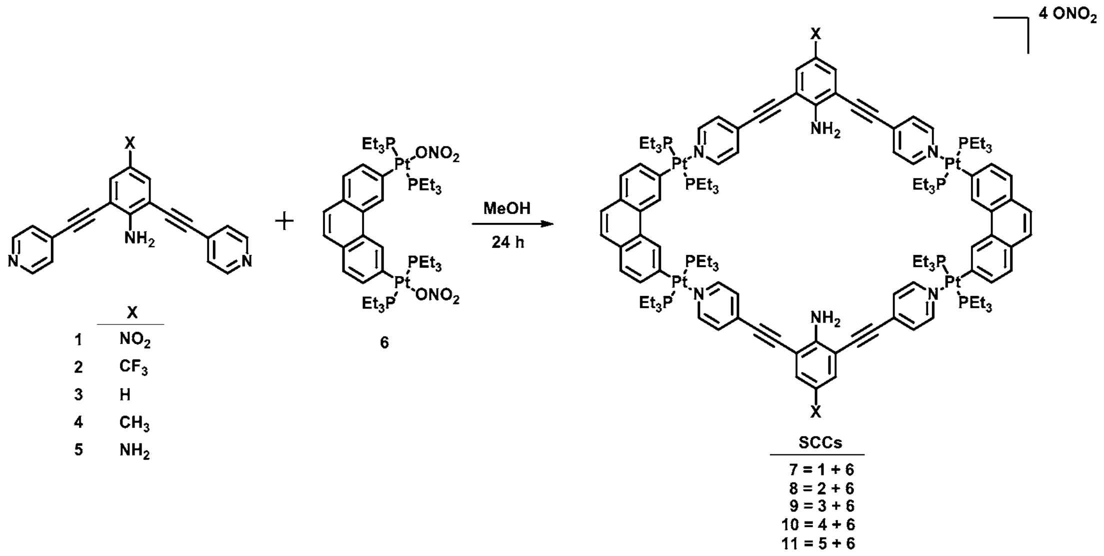
Scheme 1



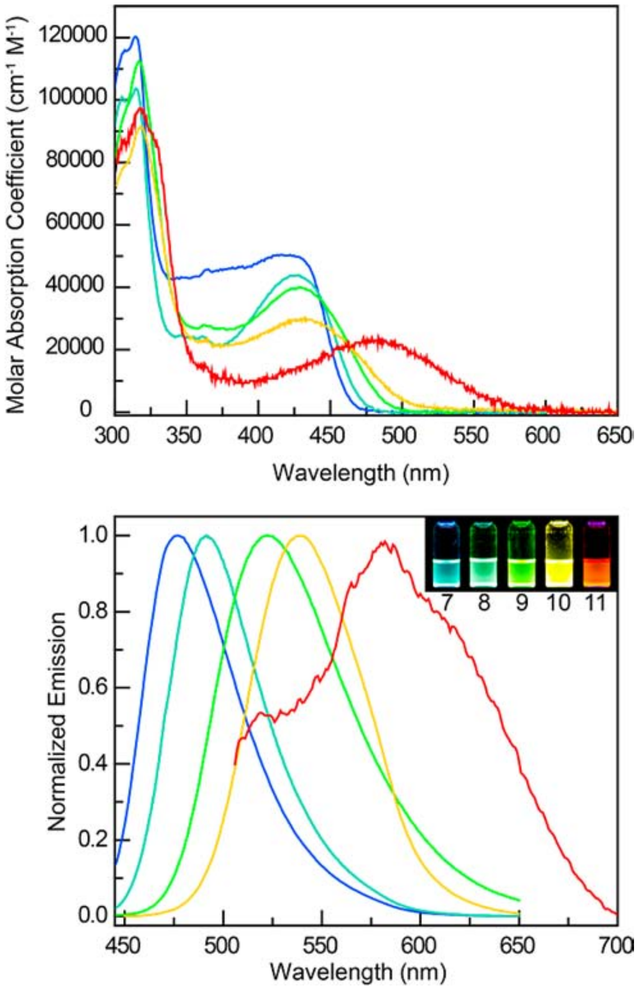


Figure 1. Absorption (top) and emission (bottom) profiles for **7** (blue), **8** (turquoise), **9** (green), **10** (yellow), and **11** (red).

Table 1. Molar Absorption Coefficients, Emission Band Maxima, and Quantum Yields for 7−11 in Aerated Methylene Chloride

	absorption bands			
SCC	$\lambda_{\max}$/nm [$\varepsilon \times 10^{-3}$, cm^{-1} M^{-1})]	λ_{exc}/nm	λ_{emiss}/nm	Φ/%^{a}
7	305 [114] *sh*, 314 [120], 420 [50.2]	420	476	1.1
8	304 [99.8] *sh*, 315 [104], 425 [43.6]	425	491	7.6
9^{b}	317 [112], 430 [39.9]	430	522	28
10	318 [91.4], 432 [29.5]	430	538	12
11	317 [97.5], 480 [23.6]	480	581	<1.0

^{a}Quantum yield was determined using quinine sulfate at 365 nm (Φ = 0.56), except for **11**, for which rhodamine 6G was utilized to determine the quantum yield (480 nm, Φ = 0.95). ^{b}Data obtained from ref 10g.

absorption band, however, seems to be sensitive to the nature of the functional group *para* to the aniline amine, and the band maximum increases while the molar absorption coefficient decreases with the electron-donating ability of the functional group *para* to the aniline amine. SCC **7** has a low-energy band maximum of 420 nm and a molar absorption coefficient of 50 200 cm^{-1} M^{-1}, while **11** has a low-energy band maximum of 480 nm and a molar absorption coefficient of 23 600 cm^{-1} M^{-1}. Figure 1 (bottom) shows the emission profiles for SCCs **7−11**, which red-shift (**7**, 476 nm to **11**, 581 nm) with increasing electron-donating ability of the functional group *para* to the aniline amine. It was observed that the quantum yield increases from **7** to **9** (Φ = 0.011 to Φ = 0.28) and then decreases from **9** to **11** (Φ = 0.28 to Φ < 0.01); the loss of quantum yield upon Pt complexation (**3**, Φ = 0.66; **9**, Φ = 0.28) was previously hypothesized to originate from increased intersystem crossing (ISC) due to the "heavy atom effect" to a nonradiative triplet state which aniline-based species are known to possess.[11] The excited states of related bis(phosphine) Pt-based endohedral amine systems, including system **9**, were previously explored and were determined not to phosphoresce in oxygen-free solvents due to a nonradiative triplet state.[12]

Interestingly, when the emission band maxima are converted to wavenumbers (cm^{-1}) and plotted against the Hammett sigma constants for the functional groups *para* to the aniline amine, a linear relationship is obtained (Figure 2).[13] This allows for specific wavelengths between 476 and 581 nm to be chosen on the basis of the Hammett σ_{para} value for a particular functional group. However, as previously noted, the quantum yields of **7−9** increase (**7**, Φ = 0.011; **9**, Φ = 0.28) while **9−11**

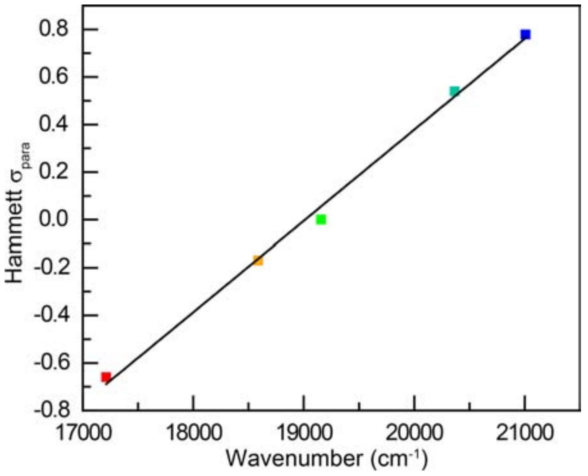


Figure 2. Hammett σ_{para} constants vs wavenumber (cm^{-1}) for **7** (blue), **8** (turquoise), **9** (green), **10** (yellow), and **11** (red). Fit to the equation $y = 0.0038x - 7.275$, with $R^2 = 0.995$.

decrease (**9**, $\Phi = 0.28$; **11**, $\Phi < 0.01$), which implies that there is an intimate relationship between the Hammett σ_{para} value and the quantum yield that is not fully understood.

The solvent effects on the absorption and emission profiles for **7**−**11** were probed using acetone, dimethylsulfoxide (DMSO), methanol, and methylene chloride; however, there was no observable trend between the systems, and there was little effect (<10 nm) on the λ_{max} for the absorption and emission profiles. As an example, the absorption and emission profiles for **9** can be found in the Supporting Information.

As a control, the steady-state absorption and emission profiles for ligands **1**−**5** in aerated DMSO were obtained, and the relevant metrics are listed in Table 2. Ligands **1**−**5** were determined to have low-energy absorption bands that range from 388 to 437 nm, with decreasing molar absorption coefficients from **1** to **5** (from 27 000 to 8100 cm^{-1} M^{-1}). The decrease in the molar absorption coefficients for the low-energy band maxima correlated with an increase in the electron-donating ability of the functional group *para* to the aniline amine. This trend also manifested itself in the emission band maxima for **2**−**5**, with **2** and **5** having emission band maxima of 442 and 480 nm, respectively. As with **7**−**11**, the quantum yield increased from **1** to **3** ($\Phi < 0.01$ to $\Phi = 0.66$) and then decreased from **3** to **5** ($\Phi = 0.66$ to $\Phi = 0.23$). Also, the molar absorption coefficient of **6** was measured in aerated methylene chloride (Supporting Information), which had multiple higher energy bands when compared to **1**−**5**; however, there was no observed emission in the visible region for **6**.

Table 2. Molar Absorption Coefficients, Emission Band Maxima, and Quantum Yields for 1−6

	absorption bands			
ligand	λ_{max}/nm [$\varepsilon \times 10^{-3}$,cm^{-1} M^{-1}]	λ_{exc}/nm	λ_{emiss}/nm	Φ/%^{a}
1	390 [27.0]	390	443, 508	<1.0
2	388 [22.8]	388	442	48
3	390 [16.7]	390	458	66
4	398 [11.2]	398	473	48
5	437 [8.1]	415	480	23
6	364 [1.1], 346 [1.6], 322 [20.1], 308 [19.0], 290 [24.0]	350	−	no emiss

^{a}Quantum yield was determined using quinine sulfate at 365 nm (Φ = 0.56).

In conclusion, tunable rhomboidal-shaped [D_2A_2] SCCs (**7**−**11**) that displayed predictable emission profiles spanning the visible region (476−581 nm) were synthesized from 2,6-bis(4ethynylpyridine)anline-based ligands (**1**−**5**). Moreover, by utilizing the linear relationship between the Hammett σ constants for the peripheral functional groups and the wavenumbers for the λ_{max} of the emission profiles, a rhomboid with a predetermined emission profile can be readily synthesized. As the fundamental science behind the quantum yields and other photophysical properties is developed, such complexes can be adapted for a number of applications such as real-time cellular monitoring of the transport, internalization, and delivery of anti-cancer therapeutics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of ligands **1**−**5** and SCCs **7**−**11**; ^{1}H and ^{31}P{^{1}H} NMR, ESI-MS, and UV/vis spectra; absorption and emission profiles during solvent study of **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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