

## Synthesis and Properties of 2-(2-Pyridyl)-1-azaazulene

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**Abstract:** The title azaazulene **3** was synthesized either by reaction of tropone with *N*-{(2-pyridyl)acetyl}pyridinium iodide in the presence of ammonium acetate or by palladium-catalyzed cross-coupling between 2-halo-1-azaazulene and 2-substituted pyridine. The compound shows relatively stronger basicity compared with 2,2'-bipyridyl. While **3** showed no emission from the S<sub>1</sub> state but from the S<sub>2</sub> state like azulene does, the protonated species of **3** exhibited emission from the S<sub>1</sub> state. Cationic metal-dependent absorption and emission relating to complexation were also studied.

*Keywords:* Basicity; UV-Vis absorption spectrum; Emission spectrum; Cross-coupling reaction; Metal complexation.

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To date, synthetic studies of pyridyl-azaazulene and -diazazulenes<sup>1</sup> which can be used a bidentate ligand like 2,2'-bipyridyl<sup>2</sup> have been limited to two cases reported by Abe et al. and Nakano et al. The former authors prepared 2-chloro-8-(2-pyridyl)-1-azaazulene (**1**)<sup>3</sup> by addition of 2-pyridyllithium to 2-chloro-1-azaazulene and subsequent oxidation, and Nakano et al. synthesized 2-(2-pyridyl)-1,3-diazazulene (**2**)<sup>4</sup> by the reaction of 2-methoxy- or 2-chlorotropone with pyridylamidine. However, their basic physical properties have not been disclosed fully and application of **1** to metal complexation is also limited. Abe et al. reported that reaction of **1** with copper ion yielded the 2:1 complex with a whole shape of the trigonal bi-pyramidal structure but not of a square plane structure probably because of steric interaction between the 3'- and 7-protons in its planar structure. Indeed, DFT calculations<sup>5</sup> predict the severe interaction in a

planar structure of **1**.<sup>6</sup> In this letter we describe the synthesis and basic physical properties, including emission property, of the title compound **3** which is expected to behave as a bidentate ligand in a different way from **1**.

<Insert Chart 1 >

The synthesis of **3** was achieved by two methods as shown in Scheme 1. One method is based on the azaazulene synthesis of Sugimura et al.<sup>7</sup> The reaction of tropone (**4**) with the ylide, generated from *N*-{(2-pyridyl)acetyl}pyridinium iodide (**5**)<sup>8</sup>, in the presence of ammonium acetate provided **3**. After an exploration of the reaction conditions in this intricate multi-step reaction, the optimal yield of **3** (58%) was realized when refluxed in acetic acid with the aid of 7.5 equivalents of ammonium acetate.<sup>10</sup> The other method is a Pd-catalyzed cross-coupling reaction between 2-halo-1-azaazulenes (**6a-c**)<sup>9</sup> and 2-substituted pyridines **7**. Results of the cross-coupling reactions are listed in Table 1. The Suzuki-Miyaura coupling<sup>11</sup> of **6** was examined with 2-pyridineboronic acid *N*-phenyldiethanolamine (NPDEA) ester<sup>12</sup> and the yields of **3** were low (entry 1-3). The Negishi coupling using 2-pyridylzinc bromide required a greater amount of the palladium catalyst and resulted in much better yields. While chloro- and bromoazaazulenes, **6a** and **6b**, were not consumed completely even in a longer reaction period (entry 4-5), reaction with iodoazaazulene **6c** proceeded smoothly, providing the highest yield (92%) of **3** (entry 6). The Stille coupling (entry 7-9) with tributylstannylpyridine **7c** completed much faster than the other couplings and provided moderate yields of **3**. In contrast to the other couplings, the Stille coupling with **6c** was hampered by formation of by-products, affording **3** in 14% yield.

<Insert Scheme 1 and Table 1>

The title compound **3** was isolated as fine red needles after sublimation and was characterized by spectroscopic and combustion analyses. Although allowing a sample of **3** to stand at room temperature under air resulted in a slight change of color from fine to dull red, the sample can be stored under inert gas atmosphere in a refrigerator without any change for at least more than a couple of months. In the UV-Vis spectrum in acetonitrile the longest wavelength absorption maximum of **3** was observed at  $\lambda_{\max} = 512$  nm which showed a bathochromic shift in less polar solvents, suggesting significant contribution of the dipolar resonance forms, **3A** and **3B**, at the ground state. A hypsochromic shift was observed in acidic solutions of **3**. In 50% H<sub>2</sub>SO<sub>4</sub> the maximum was observed at  $\lambda_{\max} = 429$  nm with a hyperchromic effect and thus the solution appeared in yellow. Mono- and diprotonated species of **3** with hydrogen bromide were also isolated.<sup>13</sup> The p*K*<sub>a</sub> values of the salts were determined by pH measurements of the solutions prepared by mixing **3** with arbitrary amounts of these salts<sup>14,15</sup> to be  $2.42 \pm 0.12$  (p*K*<sub>a2</sub>) for the proton dissociation of **3**·2H<sup>+</sup> and  $6.02 \pm 0.06$  (p*K*<sub>a1</sub>) for the dissociation of **3**·H<sup>+</sup> (Table 2). Both values are greater than the reported values of 2,2'-pyridyl,<sup>15-17</sup> *id est*, both the imino groups of **3** are stronger bases than those of 2,2'-pyridyl. The major reason can be drawn from the stabilized resonance structures<sup>18</sup> of **3A** and **3B** with the negatively charged five-membered ring. The p*K*<sub>a1</sub>

value of **3** is slightly less than that of 2-phenyl-1-azaazulene (**8**).<sup>8,19</sup> The phenomenon is rationalized by a fact that a pyridyl group shows a greater electron-withdrawing resonance effect than a phenyl group does. Therefore, the monoprotonated species **3**·H<sup>+</sup> is thermodynamically destabilized by the pyridyl group much more than **8**·H<sup>+</sup> is by the phenyl group.<sup>20</sup>

<Insert Table 2>

An outstanding feature of physical properties of **3** is its pH-dependent emission spectrum at room temperature. The free base **3** in acetonitrile showed an emission, assumed to be S<sub>2</sub> → S<sub>0</sub> relaxation, at 434 nm upon excitation of 368 nm ( $\Phi = 5.26 \times 10^{-3}$ )<sup>21</sup> and no emission upon excitation of the longest wavelength maximum of 512 nm (Fig. 1),<sup>22</sup> similarly seen in the case of azulene.<sup>23</sup> On the other hand, the diprotonated species **3**·2H<sup>+</sup> in 50% H<sub>2</sub>SO<sub>4</sub> exhibited an emission of 484 nm upon excitation of the longest wavelength maximum of 429 nm ( $\Phi = 4.10 \times 10^{-4}$ ),<sup>21</sup> assumed to be S<sub>1</sub> → S<sub>0</sub> relaxation (Fig. 2).<sup>24</sup> Noteworthy we report at a first time that 1-azaazulene shows a clear emission upon excitation of the longest wavelength absorption in acidic media at room temperature,<sup>25</sup> apart from its relatively low quantum yield.

<Insert Figure 1 and 2>

The absorption and emission spectra of **3** were found also dependent on a metal cation present in a solution. While the longest wavelength absorption maximum of **3** in the presence of a large excess amount of NaClO<sub>4</sub> in acetonitrile indicated a slight hypsochromic shift of 14 nm, the maximum of **3** in the presence of the same amount of Mg(ClO<sub>4</sub>)<sub>2</sub> showed a greater hypsochromic shift of 34 nm with a greater coefficient. In addition, while an emission at 543 nm was observed upon excitation of the longest wavelength absorption maximum of 478 nm in the presence of Mg<sup>2+</sup> ion, no emissions was observed from the S<sub>1</sub> state in the presence of Na<sup>+</sup> ion but an emission from the S<sub>2</sub> state as seen in the free base (Figs 3 and 4). These results suggest that **3** forms a rigid complex with Mg<sup>2+</sup> ion, probably in a tetrahedral shape,<sup>26</sup> but not with Na<sup>+</sup> ion.

<Insert Figure 3 and 4>

As a summary, we have synthesized a novel 1-azaazulene derivative, 2-(2-pyridyl)-1-azaazulene (**3**), either by reaction of tropone with *N*-{(2-pyridyl)acetyl}pyridinium iodide with the aid of ammonium acetate or by the cross-couplings between 2-halo-1-azaazulene and 2-substituted pyridine. The compound exhibits relatively stronger basicity and it should be emphasized that **3** showed the pH and cationic metal dependent emission spectra. Further a study on chelation of this novel ligand with various metal ions including transition metals is under a progress.

## Acknowledgements

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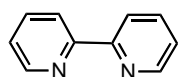
## References and Notes

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4. Nakano, H.; Sunagawa, G. *Chem. Pharm. Bull.* **1965**, *13*, 465-472.
5. DFT calculations were carried out at the B3LYP/6-31G(d) level of theory by using the Mulliken program (ver. 2.0.0, IBM Inc.).
6. Total energy difference between the planar structure with the two nitrogen atoms at the same side and the most stable structure with a dihedral angle through 1'-2'-8-8a of 148.8° is 0.21619 a.u (13.521 kcal mol<sup>-1</sup>). The distance between the 3' and 7 protons in the planar structure is 1.756 Å (175.6 pm).
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8. Polin, J.; Schmohel, E.; Balzani, V. *Synthesis*, **1998**, 321-324.
9. For the chloride and bromide, see; Nozoe, T.; Seto, S.; Matsuura, S.; Terasawa, T. *Chem. Ind.* **1954**, 1357-1358. The iodide was obtained in 66% yield from the bromide by treating with magnesium and subsequently with iodine.
10. The details of this reaction were as follows; A solution of **4** (1.06 g, 10.0 mmol), **5** (3.65 g, 11.2 mmol), and ammonium acetate (5.77 g, 75 mmol) in 100 mL of acetic acid was refluxed for 6 hr. The reaction mixture was cooled and carefully poured into a NaHCO<sub>3</sub> aq. solution, and was passed through a Celite pad. The filtrate was diluted with ethyl acetate (100 mL), and the organic layer was separated and washed with a sodium thiosulfate aq. solution and brine. After dryness over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporation gave red solids, which were chromatographed on alumina (eluted with AcOEt/hexane = 3/1) and then sublimed (150 °C/ 3 mmHg) to give 1.20 g (58% yield) of **3** as fine red needles: Mp 160-161 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 8.80 (dm, *J* = 4.8 Hz, 1H, H-6'), 8.75 (d, *J* = 9.7 Hz, 1H, H-8), 8.62 (d, *J* = 9.7 Hz, 1H, H-4), 8.57 (dm, *J* = 7.7 Hz, 1H, H-3'), 8.14 (s, 1H, H-3), 7.87 (td, *J* = 7.7, 1.8 Hz, 1H, H-4'), 7.86 (tt, *J* = 9.7, 1.1 Hz,

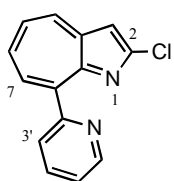
- 1H, H-6), 7.78 (tm,  $J = 9.7$  Hz, 1H, H-7), 7.65 (t,  $J = 9.7$  Hz, 1H, H-5), 7.35 (dd,  $J = 7.7, 4.8$  Hz, 1H, H-5') ppm;  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta = 112.6$  (C-3), 122.8 (C-3'), 124.0 (C-5'), 128.8 (C-5), 129.6 (C-7), 136.2 (C-4), 136.6 (C-8), 136.8 (C-4'), 137.6 (C-6), 147.9 (C-3a), 150.0 (C-6'), 153.7 (C-2'), 158.6 (C-2), 166.4 (C-8a) ppm. Found: C, 81.53; H, 4.89, N, 13.58%. Calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2$ : 81.62; H, 5.03, N, 13.43%.
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  13. Salt **3**·HBr: brownish yellow crystals, mp 223-225 °C.  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ )  $\delta = 9.36$  (d,  $J = 10.0$  Hz, 1H, H-4), 9.23 (d,  $J = 10.0$  Hz, 1H, H-8), 8.93 (d,  $J = 4.8$  Hz, 1H, H-6'), 8.72 (t,  $J = 10.0$  Hz, 1H, H-6), 8.61 (t,  $J = 10.0$  Hz, 1H, H-7), 8.54 (t,  $J = 7.3$  Hz, 1H, H-3'), 8.51 (t,  $J = 10.0$  Hz, 1H, H-5), 8.50 (s, 1H, H-3), 8.18 (td,  $J = 7.3, 1.8$  Hz, 1H, H-3'), 7.71 (dd,  $J = 7.3, 4.8$  Hz, 1H, H-5'), ppm; IR (KBr)  $\nu = 3370\text{s}, 3052\text{s}, 1569\text{s}, 1432\text{s}, 1332\text{s}, 790\text{s}, 742\text{s}$   $\text{cm}^{-1}$ . Found: C, 54.24; H, 4.23, N, 8.82%. Calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{Br}\cdot\tilde{\text{i}}$   $\text{H}_2\text{O}$ : 54.30; H, 4.39, N, 9.05%. The distinctive change of  $^1\text{H-NMR}$  signals of the salt **3**·HBr in  $\text{DMSO-}d_6$  compared with those of the free base indicates that it exists mainly as the monoprotonated species in the solution. Salt **3**·2HBr: Lemon yellow crystals, mp 219-221 °C. IR (KBr)  $\nu = 3311\text{s}, 3078\text{s}, 2611\text{m}, 1614\text{s}, 1456\text{s}, 1440\text{s}, 787\text{s}$   $\text{cm}^{-1}$ . Found: C, 45.62; H, 3.25, N, 7.48%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{Br}_2$ : 45.68; H, 3.29, N, 7.61%. NMR signals of **3**·2HBr in  $\text{DMSO-}d_6$  were very similar with those of **3**·HBr, proving that dissociation of **3**·2H $^+$  provided **3**·H $^+$  under the conditions. See followings for NMR data of **3**·2H $^+$ ;  $^1\text{H-NMR}$  (50%  $\text{D}_2\text{SO}_4$  in  $\text{D}_2\text{O}$ , DSS as an internal standard)  $\delta = 9.47$  (d,  $J = 10.0$  Hz, 1H, H-4), 9.30 (d,  $J = 10.0$  Hz, 1H, H-8), 9.03 (d,  $J = 6.3$  Hz, 1H, H-6'), 8.94 (m, 2H, H-6, 4'), 8.77 (d,  $J = 8.0$  Hz, 1H, H-3'), 8.75 (t,  $J = 10.0$  Hz, 1H, H-7), 8.69 (t,  $J = 10.0$  Hz, 1H, H-5), 8.45 (s, 1H, H-3), 8.32 (dd,  $J = 7.3, 6.3$  Hz, 1H, H-5') ppm.
  14. Measurements were carried out in the presence of 0.5 M  $\text{NaClO}_4$  in 50% aqueous ethanol.
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  21. The quantum yield of **3** was obtained with anthracene as a standard ( $\Phi = 2.7 \times 10^{-1}$ ) in ethanol and that of **3**·2H $^+$  with 2-aminopyridine as a standard ( $\Phi = 3.7 \times 10^{-1}$ ) in 0.5M  $\text{H}_2\text{SO}_4$ .
  22. It was reported that 2-phenyl-1-azaazulene exhibited fluorescence from the  $\text{S}_1$  state under

- special circumstances; Burke, F. P.; Eslinger, D. R.; Small, G. J. *J. Chem. Phys.* **1975**, *63*, 1309-1310. For emission spectra of 1,3-diazaazulene, see; Jinguji, M.; Ashizawa, M.; Nakazawa, T.; Tobita, C.; Hikida, T.; Mori, Y. *Chem. Phys. Lett.*, **1985**, *121*, 400-404.
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24. The monoprotonated species  $\mathbf{3}\cdot\text{H}^+$  also exhibited the  $S_1 \rightarrow S_0$  emission with a quantum yield of 0.027, which was measured with 2-aminopyridine as a standard ( $\Phi = 0.48$ ) in acetonitrile.
25. We also found that 2-phenyl-1-azaazulene (**8**) behaved similarly.
26. The Job plot of **3** with  $\text{Mg}(\text{ClO}_4)_2$  using absorption changes indicated the binding mode of two molecules of **3** to one of  $\text{Mg}^{2+}$  ion.

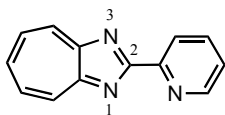
## Chart 1



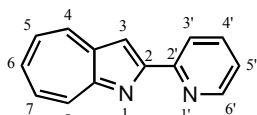
2,2'-bipyridyl



1

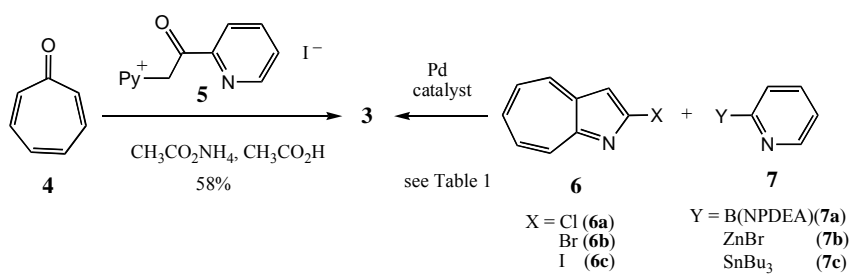


2



3

**Scheme 1. Synthetic methods of 3.**



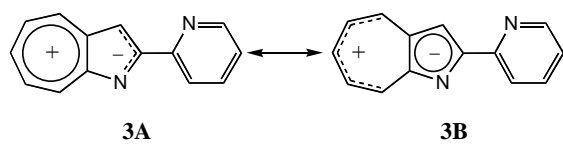


**Table 1.** Results of cross-coupling reactions of 2-halo-1-azaazulene **6**.

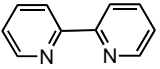
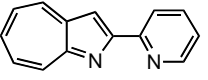
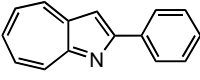
entry	<b>6</b>	<b>7</b>	reaction conditions	yield (%) of <b>3</b> <sup>a</sup>	recovery of <b>6</b>
1	<b>6a</b>	<b>7a</b> <sup>b</sup>	5%Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> , CuI, Cs <sub>2</sub> CO <sub>3</sub> , THF, refl, 4 h	0	95
2	<b>6b</b>	<b>7a</b> <sup>b</sup>	5%Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> , CuI, Cs <sub>2</sub> CO <sub>3</sub> , THF, refl, 4 h	20 (22)	7
3	<b>6c</b>	<b>7a</b> <sup>b</sup>	5%Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> , CuI, Cs <sub>2</sub> CO <sub>3</sub> , THF, refl, 4 h	25	0
4	<b>6a</b>	<b>7b</b> <sup>c</sup>	10%Pd(PPh <sub>3</sub> ) <sub>4</sub> , THF, 60° C, 48 h	47 (68)	32
5	<b>6b</b>	<b>7b</b> <sup>c</sup>	10%Pd(PPh <sub>3</sub> ) <sub>4</sub> , THF, 60° C, 48 h	51(80)	36
6	<b>6c</b>	<b>7b</b> <sup>c</sup>	10%Pd(PPh <sub>3</sub> ) <sub>4</sub> , THF, 60° C, 48 h	92	0
7	<b>6a</b>	<b>7c</b> <sup>d</sup>	5%Pd(PPh <sub>3</sub> ) <sub>4</sub> , CuO, DMF, 120 °C, 3 h	44	0
8	<b>6b</b>	<b>7c</b> <sup>d</sup>	5%Pd(PPh <sub>3</sub> ) <sub>4</sub> , CuO, DMF, 120 °C, 3 h	47	0
9	<b>6c</b>	<b>7c</b> <sup>d</sup>	5%Pd(PPh <sub>3</sub> ) <sub>4</sub> , CuO, DMF, 120 °C, 3 h	14 <sup>e</sup>	0

<sup>a</sup>The yields in parentheses are based on the consumed starting material. <sup>b</sup> An excess of the reagent (3 eq.) were used. <sup>c</sup> An excess of the reagent (2.7 eq.) were used. <sup>d</sup> A slightly excess of the reagent (1.2 eq.) was used. <sup>e</sup>The desired product **3** was obtained with a mixture of by-products whose structures were not clarified yet.

**Chart 2**

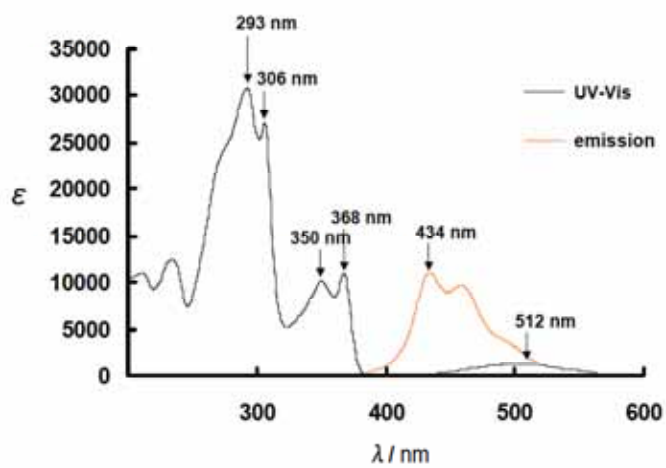


**Table 2.** The  $pK_a$  values of 2,2'-bipyridyl, **3**, and **8**.

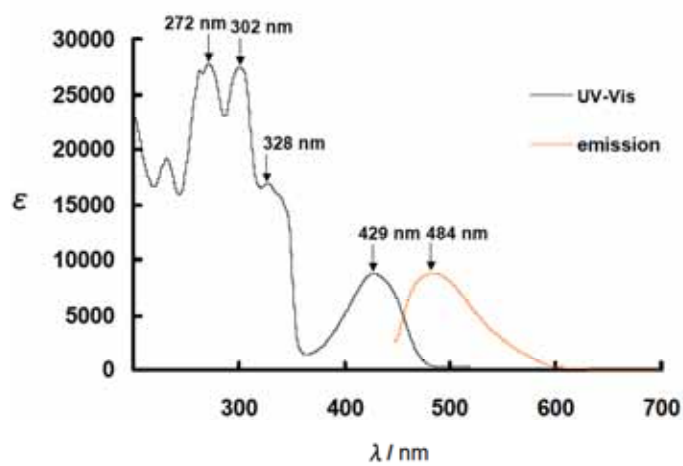
amines	$pK_{a1}$	$pK_{a2}$
	4.34 <sup>a</sup>	-0.20 <sup>a</sup>
2,2'-bipyridyl	4.12 <sup>b</sup>	-0.52 <sup>c</sup>
	<b>3</b>	6.02 <sup>d</sup>
	<b>8</b>	6.81 <sup>d</sup>

<sup>a</sup> Taken from ref. 16. <sup>b</sup> Taken from ref. 15.  
<sup>c</sup> Taken from ref. 17. <sup>d</sup> Measured in this study.

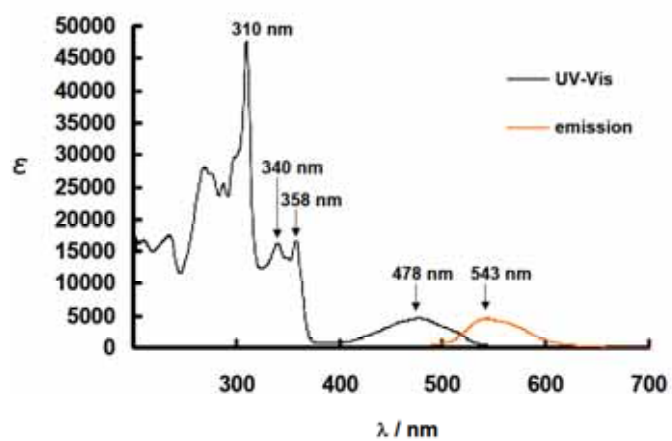
**Figure 1.** The UV-Vis absorption and normalized emission spectra of **3** in CH<sub>3</sub>CN.



**Figure 2.** The UV-Vis absorption and normalized emission spectra of **3** in 50% H<sub>2</sub>SO<sub>4</sub>.



**Figure 3.** The UV-Vis absorption and normalized emission spectra of **3** in the presence of magnesium perchlorate (1000 eq. to **3**).



**Figure 4.** The UV-Vis absorption and normalized emission spectra of **3** in the presence of sodium perchlorate (1000 eq. to **3**).

