Effect of branching in remote substituents on light emission and stability of chemiluminescent acridinium esters

Supplementary Material

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1. HPLC traces, $^1$H-NMR and high resolution mass spectra of synthetic intermediates and acridinium esters of Figures 4 and 5.
Figure S1a. HPLC trace of the crude reaction mixture showing a pair of diastereomers for compound 3 eluting at 4.6 and 4.8 minutes. Peak eluting at 4.4 minutes is related to the ionic liquid and peak eluting at 7.3 min is dibenzo-18-crown-6. HPLC conditions: Phenomenex, Kinetex, C$_{18}$, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S1b. HPLC trace of compound 3 showing a pair of diastereomers after purification of the mixture. During purification, some loss of the earlier eluting diastereomer was observed. HPLC conditions: Phenomenex, Kinetex, C_{18}, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S1c. HPLC trace of compound 3 after purification showing the early eluting diastereomer. HPLC conditions: Phenomenex, Kinetex, C18, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S1d. $^1$H NMR of compound 3 in CF$_3$COOD (earlier eluting diastereomer, refer to Figure S1c).
Figure S1e. HRMS of compound 3 (earlier eluting diastereomer, refer to Figure S1c).
Figure S1f. HPLC trace of compound 3 after purification showing the later eluting diastereomer. HPLC conditions: Phenomenex, Kinetex, C18, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S1g. $^1$H NMR of compound 3 in CF$_3$COOD (later eluting diastereomer, refer to Figure S1f).
Figure S1h. HRMS of compound 3 (later eluting diastereomer, refer to Figure S1f).
Figure S2a. HPLC trace of compound 4 showing a pair of diastereomers. HPLC conditions: Phenomenex, Kinetex, C18, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm. As observed previously during purification of compound 3, purification of 4 resulted in some loss of the earlier eluting diastereomer due to closely eluting impurities.
Figure S2b. $^1$H NMR of compound 4 in CF$_3$COOD.
Figure S2c. HRMS of compound 4.
Figure S3a. HPLC trace of compound 5 showing a pair of diastereomers. HPLC conditions: Phenomenex, Kinetex, C18, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S3b. $^1$H NMR of compound 5 in CF$_3$COOD.
Figure S3c. HRMS of compound 5.
Figure S4a. HPLC trace of compound 7. HPLC conditions: Phenomenex, Kinetex, C18, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S4b. $^1$H NMR of compound 7 in CDCl$_3$
Figure S4c. HRMS of compound 7
Figure S5a. HPLC trace of compound 8. HPLC conditions: Phenomenex, Kinetex, C18, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S5b. $^1$H NMR of compound 8 in CF$_3$COOD.
Figure S5c. HRMS of compound 8.
Figure S6a. HPLC trace of compound 9. HPLC conditions: Phenomenex, Kinetex, C18, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S6b. $^1$H NMR of compound 9 in CD$_3$COOD.
Figure S6c. HRMS of compound 9.
Figure S7a. HPLC trace of compound 10. HPLC conditions: Phenomenex, Kinetex, C<sub>18</sub>, 2.6 micron, 50 x 4.6 mm column, 10 minute gradient of 10→90% MeCN/water (each with 0.05% TFA), flow = 1 ml/minute, UV detection at 260 nm.
Figure S7b. $^1$H NMR of compound 10 in CD$_3$COOD.
Figure S7c. HRMS of compound 10