Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Supporting Information**

# Unusual Temperature-Sensitive Excimer Fluorescence from Discrete π-π Dimer Stacking of Anthracene in a Crystal

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# Contents

## SI. Experimental Section

***General Methods*:**

All the reagents and solvents used for the measurements were purchased from Aldrich and Acros companies and used without further purification. Single crystals of 2-TA-AN, 1-TA-AN, and mTPA-9-AN are prepared according to previous reports.[1, 2] The $^{1}$H-nuclear magnetic resonance (NMR) spectra were recorded on an AVANCZ 500 spectrometers at 298 K by utilizing deuterated dimethyl sulfoxide (DMSO) as solvents and tetramethylsilane (TMS) as a standard. The fluorescent spectra and lifetimes were carried out with an Edinburgh FLS-980 with an EPL-375 optical laser using the programmed temperature method. "The programmed temperature method" means the changing of temperature is automatic through programmed design rather than manual control, and the temperature is gradually increased. The diffraction experiments under ambient conditions were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-Kα and control Software using the RAPID AUTO at 100 K. Crystal structure was solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS programs.

## SII. Figures and Tables

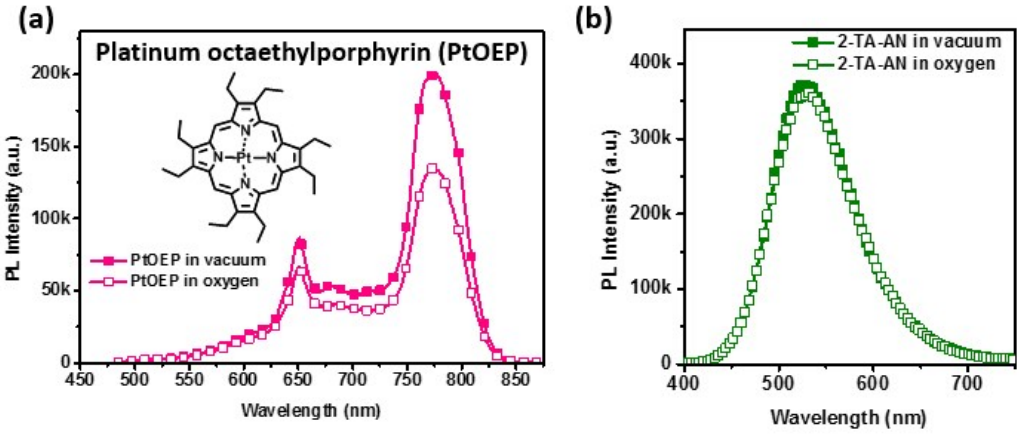


**Figure S1.** PL spectra of (a) PtOEP powder and (b) 2-TA-AN crystalline powder in vacuum and air. Herein, PtOEP as a comparison with 2-TA-AN, is metal complex whose luminescent intensity is sensitive to oxygen. This phenomenon also demonstrates that the emission from 2-TA-AN crystalline powder is fluorescence rather than phosphorescence.

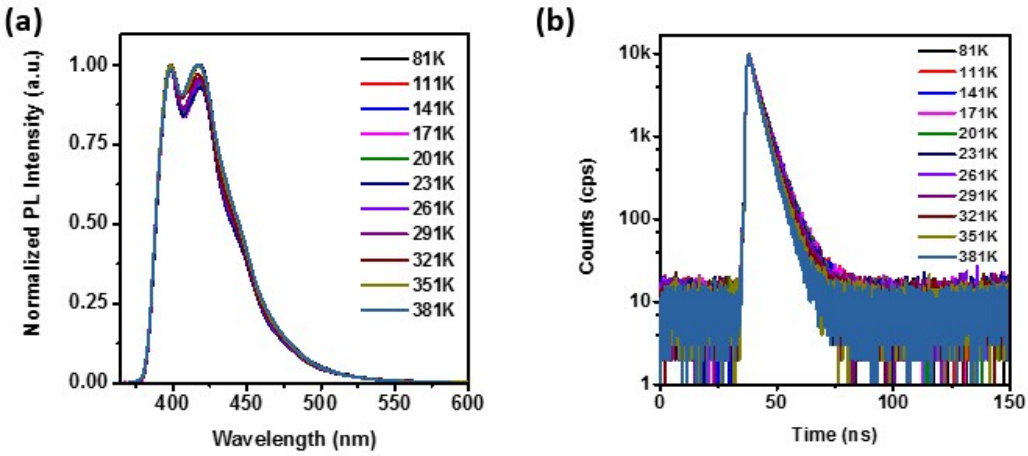


**Figure S2.** (a) PL spectra and (b) time-resolved spectra of 1 wt % 2-TA-AN in polymethyl methacrylate (PMMA) with the increasing temperature.

**Table S1.** The lifetimes of 2-TA-AN in 1 wt % film at different temperature.

| Temperature (K) | lifetimes (ns) |
|---|---|
| 81 | 4.22 |
| 111 | 4.55 |
| 141 | 4.54 |
| 171 | 4.53 |
| 201 | 4.46 |
| 231 | 4.39 |
| 261 | 4.30 |
| 291 | 4.20 |
| 321 | 4.06 |
| 351 | 3.88 |
| 381 | 3.65 |

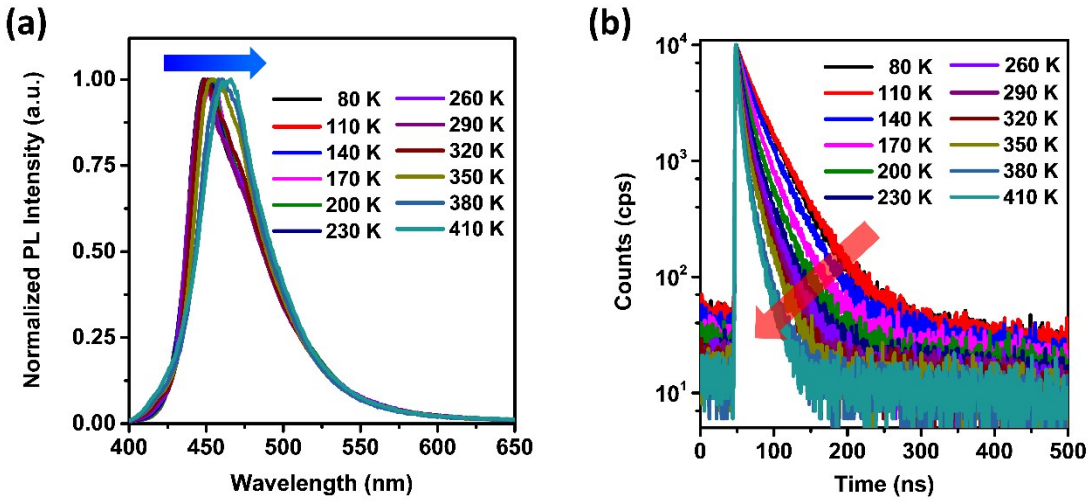


**Figure S3.** (a) PL spectra and (b) time-resolved spectra of 1-TA-AN crystal with the increasing temperature.

**Table S2.** The lifetimes of 1-TA-AN crystal at different temperature.

| Temperature (K) | $\tau_1$ (ns) | $\tau_2$ (ns) |
|---|---|---|
| 80 | 20.98 (48.07%) | 42.47 (51.93%) |
| 110 | 19.68 (37.80%) | 40.58 (62.20%) |
| 140 | 18.55 (50.36%) | 38.52 (49.64%) |
| 170 | 14.42 (54.70%) | 35.05 (45.30%) |
| 200 | 10.49 (47.76%) | 29.48 (52.24%) |
| 230 | 8.28 (47.22%) | 26.3 (52.78%) |
| 260 | 6.89 (47.22%) | 24.29 (52.78%) |
| 290 | 6.00 (48.37%) | 22.80 (51.63%) |
| 320 | 5.28 (47.35) | 20.45 (52.65%) |
| 350 | 4.92 (46.52%) | 19.21 (53.48%) |
| 380 | 4.37 (55.80%) | 16.32 (44.20%) |
| 410 | 3.45 (47.06%) | 13.40 (52.94%) |

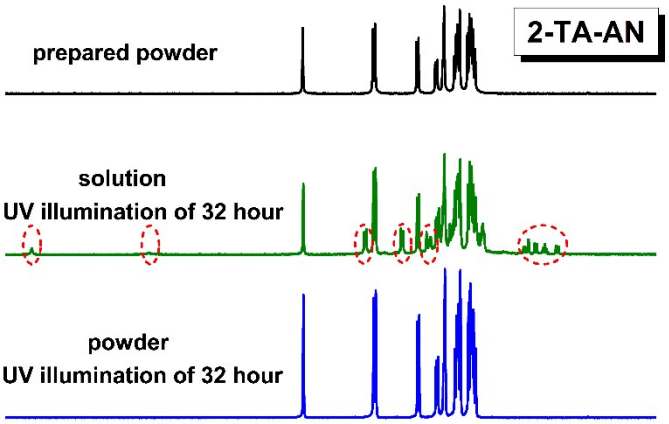


**Figure S4.** NMR spectra of 2-TA-AN compound.

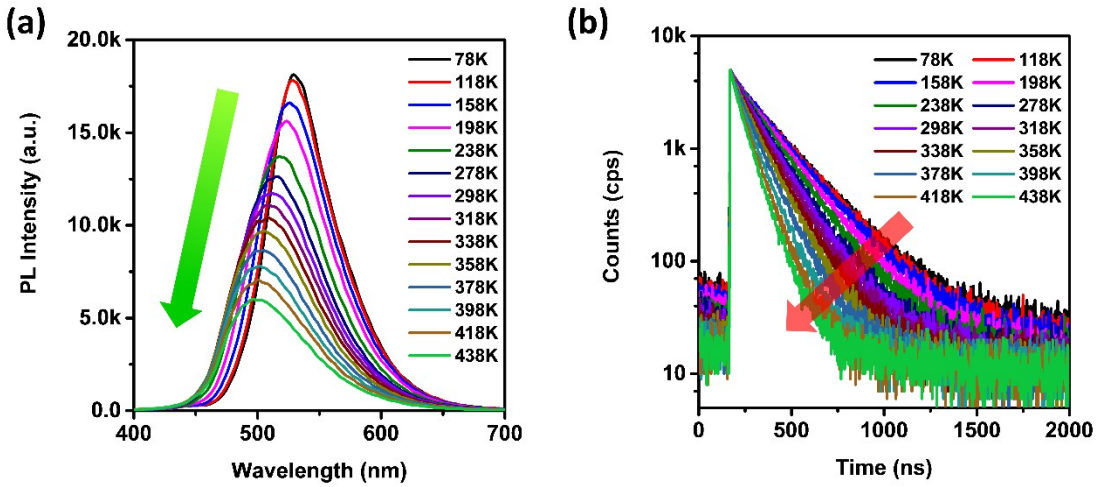


**Figure S5.** (a) PL spectra and (b) time-resolved spectra of mTPA-9-AN crystal with the increasing temperature.

**Table S3.** The lifetimes of mTPA-9-AN crystal at different temperature.

| Temperature (K) | lifetimes (ns) |
|---|---|
| 78 | 231 |
| 118 | 224 |
| 158 | 214 |
| 198 | 199 |
| 238 | 182 |
| 278 | 165 |
| 298 | 155 |
| 318 | 146 |
| 338 | 136 |
| 358 | 126 |
| 378 | 113 |
| 398 | 99 |
| 418 | 89 |
| 438 | 79 |

**Table S4.** Crystal data and structure refinement parameters of 2-TA-AN at 100 K.

| Unit cell parameters | 2-TA-AN |
|---|---|
| crystal color | yellow |
| empirical formula | $C_{26}H_{16}S_2$ |
| formula weight | 392.51 |
| $T$ [K] | 100 |
| crystal system | monoclinic |
| space group | C 2/c |
| $a$ [Å] | 16.8912(5) |
| $b$ [Å] | 11.8970(5) |
| $c$ [Å] | 19.6308(7) |
| $\alpha$ [°] | 90 |
| $\beta$ [°] | 104.361(2) |
| $\gamma$ [°] | 90 |
| $V$ [Å$^3$] | 3821.6(2) |
| $Z$ | 8 |
| F(000) | 1632 |
| density [g/cm$^3$] | 1.364 |
| $\mu$ [mm$^{-1}$] | 0.287 |
| reflections collected | 16822 |
| unique reflections | 3920 |
| $R$ (int) | 0.0267 |
| GOF | 1.106 |
| $R_1$ [$I>2\sigma(I)$] | 0.0384 |
| $\omega R_2$ [$I>2\sigma(I)$] | 0.0889 |
| $R_1$ (all data) | 0.0430 |
| $\omega R2$ (all data) | 0.0912 |
| CCDC number | 1914211 |

## SIII. References


1. H. Liu, L. Yao, B. Li, X. Chen, Y. Gao, S. Zhang, W. Li, P. Lu, B. Yang and Y. Ma, *Chem. Commun.,* 2016, **52**, 7356-7359.
2. Y. Shen, H. Liu, S. Zhang, Y. Gao, B. Li, Y. Yan, Y. Hu, L. Zhao and B. Yang, *J. Mater. Chem. C*, 2017, **5**, 10061-10067.