Electronic Supplementary Information

A highly luminescent spiro-anthracenone-based organic light-emitting diode through thermally activated delayed fluorescence

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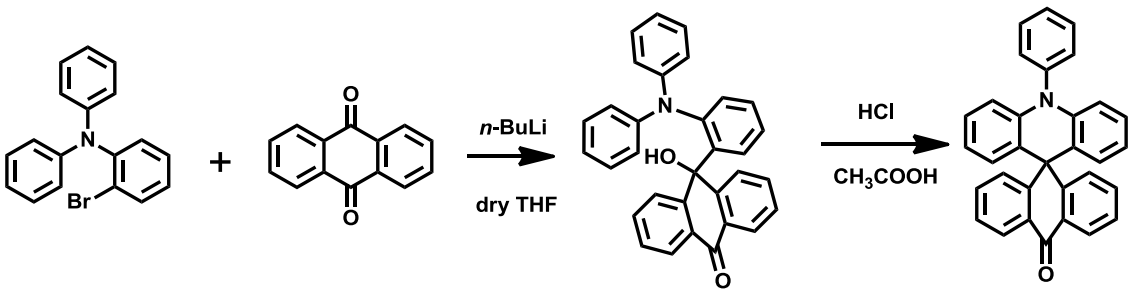
Contents

1. Synthesis of ACRSA



n-BuLi (1.6 M in hexane, 14.6 mL, 23.3 mmol) was added to a solution of 2-bromotriphenylamine (7.54 g, 23.3 mmol) in dry THF (180 mL) at -78°C. The mixture was stirred for 1.5 h at -78°C. Anthraquinone (4.3 g, 21.2 mmol) was added to the reaction solution, which was then stirred for 1 day at 0°C. The reaction mixture was extracted into chloroform. The organic layer was dried over $MgSO_4$, filtered, and then concentrated *in vacuo*. After purification by column chromatography on silica gel using chloroform as the eluent, a yellow solid was obtained. The resulting product (3.21 g, 7.09 mmol), acetic acid (55 mmol), and HCl (5.5 mL) were stirred for 4 h under reflux. The reaction mixture was filtered, and then the product was extracted into chloroform. The organic layer was dried over $MgSO_4$, filtered, and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using chloroform as the eluent and subsequent reprecipitation. The residue was further purified by sublimation (0.90 g, yield: 8.9%). ^{1}H NMR (500 MHz, $CDCl_3$) 6.32 (t) 2H, 6.49 (d) 2H, 6.58 (t) 2H, 6.89 (t) 2H, 7.35 (t) 2H, 7.41 (d) 2H, 7.5 (m) 4H, 7.60 (t) 2H, 8.40 (d) 2H. ESI-Mass $[M]^+$: Calcd. for $C_{32}H_{22}NO$: 436.16. Found: 436.19. Anal. calcd (%) for $C_{32}H_{21}N$: C, 88.25; H, 4.86; N, 3.22. Found: C, 88.34; H, 4.83; N, 3.21.

2. Experimental details

Neat ACRSA and ACRSA:host (host: TAPC, mCP, DPEPO, and UGH-2) films were fabricated by thermal deposition. Film thickness was monitored *in situ* by an oscillating quartz thickness monitor during thermal deposition. Fluorescence and thermally activated delayed fluorescence (TADF) characteristics were measured under vacuum (4×10^{-1} Pa) using a streak camera system (C4334; Hamamatsu Co.). The temperature dependence of photoluminescence (PL) was measured using a streak camera system (C4334; Hamamatsu Co.) equipped with a cryostat (GASESCRT-006-2000; Iwatani Co.). A nitrogen gas laser (MNL200; Lasertechnik Berlin, Germany) with an excitation wavelength of 337 nm was used. PL quantum efficiency was measured using an integrating sphere system (C9920; Hamamatsu Co.) with a multichannel spectrometer (PMA-11; Hamamatsu Co.). Current density-voltage (*J*-*V*) characteristics were measured using a

semiconductor parameter analyzer (HP4155C; Agilent Co.) with an optical power meter (Model 1835-C; Newport).

3. Experimental data

3-1. Prompt and delayed spectra of ACRSA in DPEPO doped film and in toluene solution.

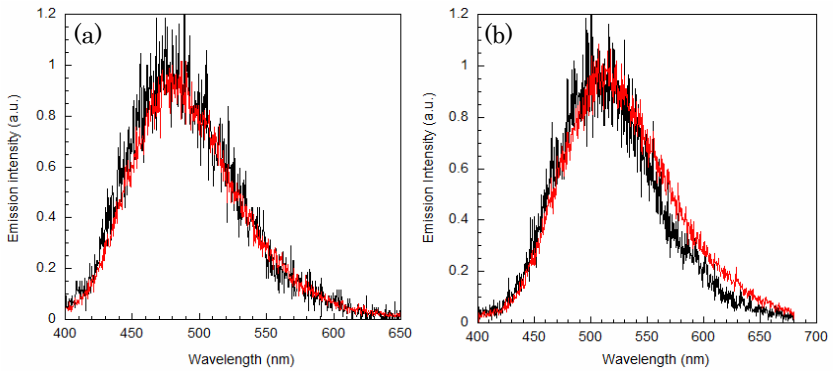


Fig. S1 PL spectra of a 9wt% ACRSA:DPEPO film (a) and ACRSA in toluene solution (b) showing a prompt component (black line, delay time = 0 s) and a delayed component (red line, delay time = 1 μs).

3-2. Transient PL decay profiles of ACRSA in toluene solution

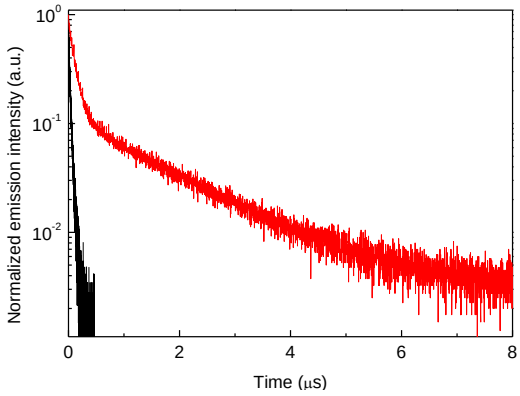


Fig. S2 Transient PL decay of ACRSA in 10^{-5} M toluene solution. Black and red lines show the profile before and after argon bubbling, respectively.

3-3 Absorption and excitation spectra of ACRSA in toluene solution

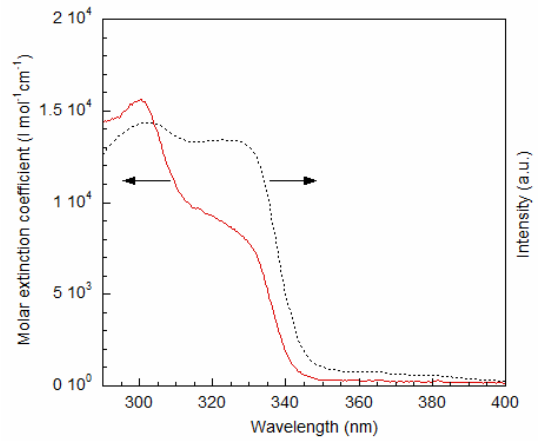


Fig. S3 Absorption and excitation spectra (detection emission wavelength = 504 nm) of ACRSA in 10^{-5} M toluene solution.

3-4. Temperature dependence of PL efficiency of a ACRSA neat film and a 9wt% ACRSA: DPEPO film

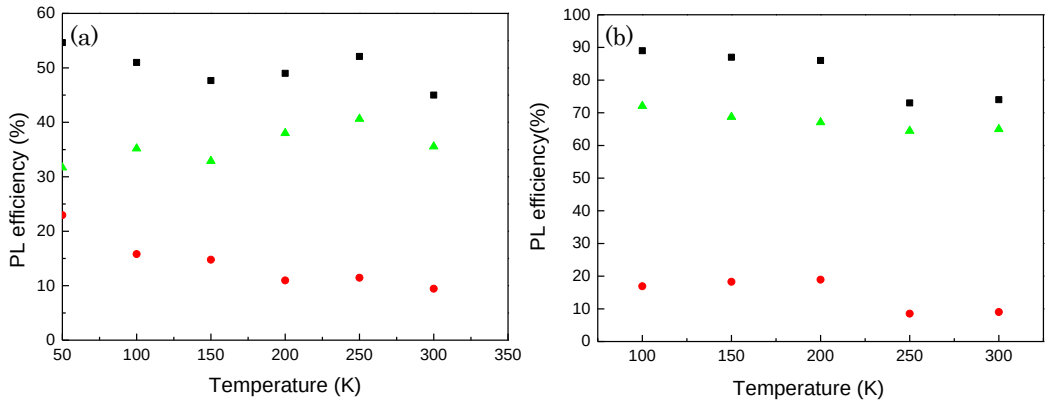


Fig. S4 Temperature dependence of the total PL (Φ_{PL}): black squares, prompt fluorescence (Φ_{prompt}): red circles, and delayed fluorescence ($\Phi_{delayed}$): green triangles of a ACRSA neat film (a) and a 9wt% ACRSA:DPEPO film (b).

3-5. Fluorescence and phosphorescence spectrum of a ACRSA neat film and a 9wt% ACRSA: DPEPO film

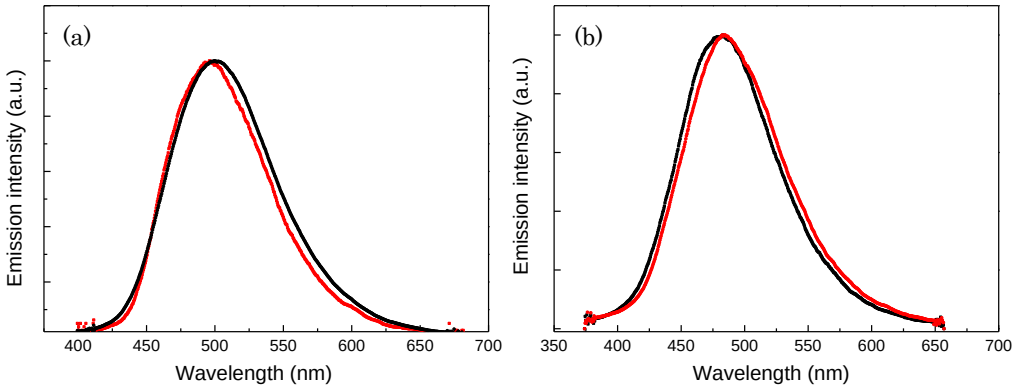


Fig. S5 Fluorescence (black line, measured at 300 K) and phosphorescence (red line, measured at 7 K) spectra of a ACRSA neat film (a) and a 9wt% ACRSA: DPEPO film (b).

4. ^{1}H NMR spectrum of ACRSA

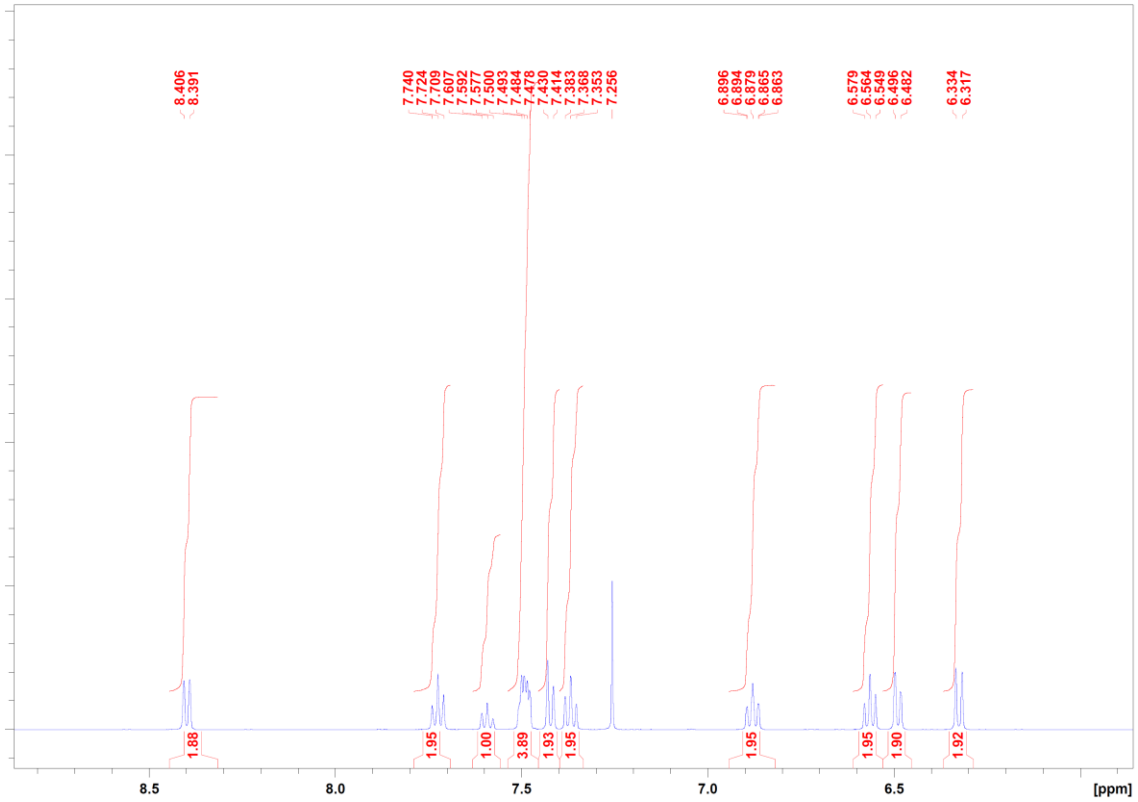


Fig. S6 ^{1}H NMR spectrum of ACRSA

5. ESI-Mass spectrum of ACRSA

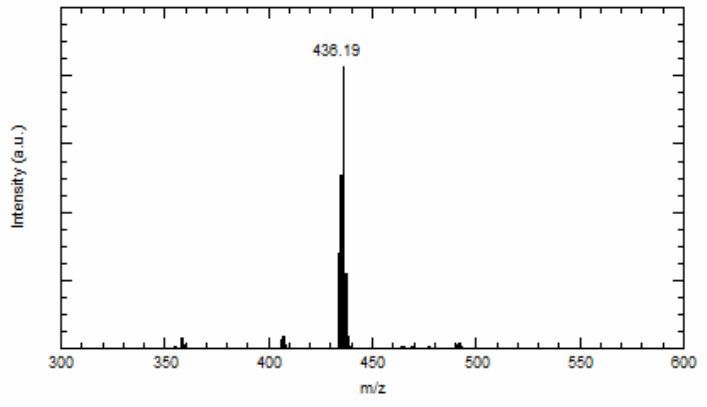


Fig. S7 ESI-Mass spectrum of ACRSA

6. Complete reference 12

12 Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz and J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.