

## Supporting Information

### Electrogenerated Chemiluminescence Soliton Waves in Conjugated Polymers

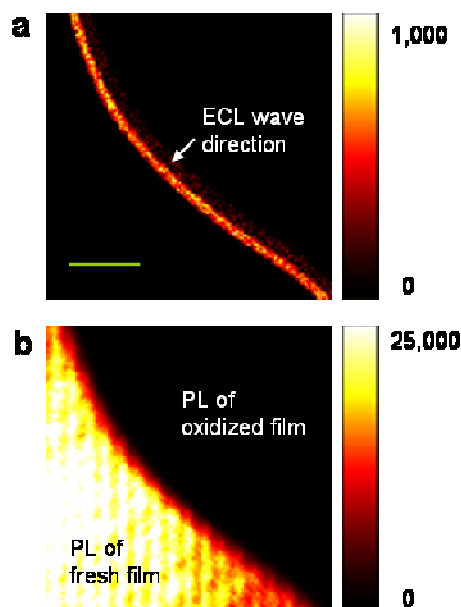
Ya-Lan Chang, Rodrigo E Palacios, Jiun-Tai Chen, Keith J. Stevenson, Song Guo,  
William M. Lackowski, and Paul F. Barbara<sup>\*</sup>

Center for Nano and Molecular Science and Technology, University of Texas, Austin,  
Texas 78712, USA

<sup>\*</sup>Correspondence should be addressed to PFB ([p.barbara@mail.utexas.edu](mailto:p.barbara@mail.utexas.edu))

### Photoluminescence quenching

Additional evidence that the propagation of the ECL wave is due to oxidation of the conjugated polymer is found in simultaneous imaging of the photoluminescence (PL, i.e. fluorescence excited by a 488 nm laser) during the EC experiment. The data (see Fig. S1 in Supplementary Information) show that in front of the ECL wave, the PL of F8BT is unchanged from non-oxidized film, while, in contrast, immediately behind the ECL wave, the fluorescence is more than 99.9% quenched (our detection limit). This suggests at least 10% of oxidation of the thin-film polymer region behind the wave, but  $\ll$  1% of oxidation in front of the wave. ( $P^+$  is a highly efficient fluorescence quencher, and even 1% of oxidation would be easily observable in the fluorescence imaging experiments.<sup>1,2</sup>) It is also interesting to note that the PL imaging technique allows for the probing of the spatial evolution of the oxidation of the film without the need of generating ECL. Employing this approach we have observed that in the absence of TPA (and as a result no ECL) the oxidation still exhibited wave-like propagation. Without TPA, however, the speed of the oxidation wave is considerably more rapid. When TPA is present  $P^+$  is neutralized by the hole transfer from  $P^+$  to the neutral and radical forms of TPA, effectively reducing the net polymer oxidation rate and as a result the wave propagation speed.



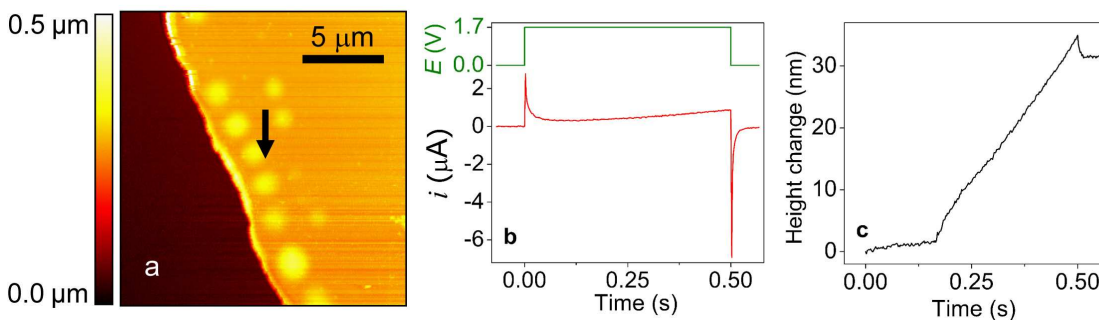
**Figure S1 | Photoluminescence (PL) quenching when a free ECL wave propagates.**

A 250 nm-thick F8BT film is in an EC cell containing an MeCN solution of 0.1 M LiClO<sub>4</sub> and 0.1 M TPA. A potential step of 1.5 V is applied during the image acquisition. **a**, An ECL image acquired at 6.4 s after the start of 1.5 V without laser excitation. **b**, An PL+ECL image acquired at 6.6 s after the start of 1.5 V with laser excitation (7 mW/cm<sup>2</sup>, 488 nm). Both images are acquired with an integration time of 100 ms. The intensity scale (unit: counts) is shown at the right side of each image. The scale bar is 50  $\mu$ m.

## AFM experiments

Direct evidence for oxidation-induced swelling due to the EC oxidation is given in Fig. S2. In this experiment, an ECL free wave is generated in an open EC cell with an AFM tip positioned  $\sim 3 \mu$ m away from the triggering scratch (indicated by the arrow in Fig. S2a) in the 250 nm film. After 15 repeated pulse sequences, an AFM image is recorded with the tip penetrating the solution (Fig. S2a). The image reveals that the scratch passes entirely through the planar F8BT film exposing the ITO electrode, and pile-up of polymer along the scratch edge was originally in the scratched region. When the first potential sequence (green curve in Fig. S2b) is applied on the pristine cell, the current (Fig. S2b) and height change (Fig. S2c) of the film are monitored simultaneously. The rapid current increase immediately after the potential step from 0 V to +1.7 V

primarily results from the co-oxidization of TPA on bare ITO and F8BT. The rapid current decrease appearing after 0.5 s as the potential is stepped back to 0 V is due to the re-reduction of F8BT. During the first 0.5 s at +1.7 V the film increases by  $\sim 35$  nm, or 15%. The actual swelling at the time the ECL wave passes the tip (i.e.  $< 0.1$  s) is below our resolution (2 nm) indicating that very little solvent is required for complete fluorescence quenching and wave propagation. After 15 repeated pulses, some buckles appear on the film near the scratch edge suggesting the swelling of F8BT due to penetration of solvent and ions. When the potential is held at +1.7 V for an extended period ( $> 60$  s) the film continues to swell, and ultimately buckle and delaminate, due presumably to the stress in the film created by the EC induced swelling.

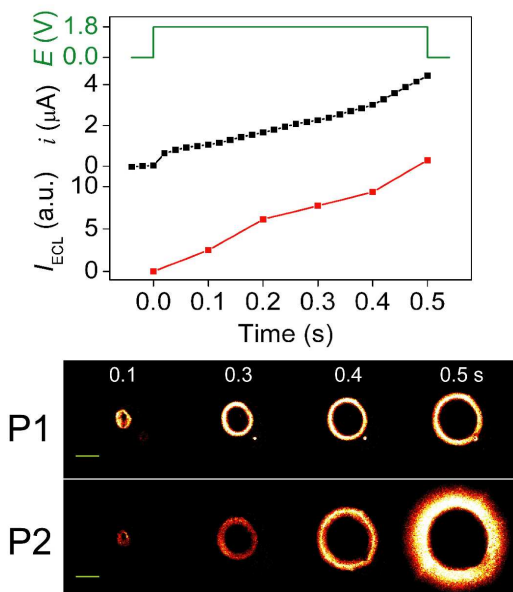


**Figure S2 | AFM data on ECL wave propagation.** (a) The AFM image of the 250 nm F8BT film with a scratch made by an NSOM tip is recorded after 15 repeated pulse sequences of 0 V for 10 s, +1.7 V for 0.5 s, and 0 V for 4.5 s. At the first sequence, the current profile (b) and the height change (c) of the F8BT film (at the position indicated by the arrow in a) are collected simultaneously.

### Retriggerable ECL free waves

Our proposed mechanism is consistent with the observation that the ECL wave speed increases strongly with the magnitude of applied potential due to the increased rate of EC oxidation as shown in Fig. S3. The mechanism is also supported by the correlation between the curves of EC current vs. time and ECL intensity vs. time during the first pulse (P1). When the ECL wave is propagating, the EC current increases due to oxidization of F8BT. When a second pulse (P2) is applied after holding the potential at 0

V for 4 s, a new ECL wave is retriggered. We note that the second wave actually propagates at a faster speed than the first wave, probably due to the residual solvent in the film.



**Figure S3 | Retriggerable ECL free waves launched by a scratch.** The current profile and integrated ECL intensity at the first applied pulse (P1, green curve) on a ~ 250 nm F8BT film with a scratch made by an NSOM tip are shown in the top panel. After a potential step of 0 V for 4 s, a repeated pulse (P2) is applied. ECL images during P1 and P2 at different times after the potential steps to +1.8 V are shown in the bottom panel. The integration time is 100 ms and the scale bars are 50  $\mu\text{m}$ .

### Detailed figure processing

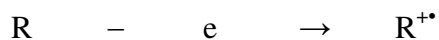
In Figure 2c, the 3D image is rendered by ImageJ with an oblique tilt along y-axis and a 0.25 z-ratio. Each light pixel is drawn as a line. The relative intensity profiles are appropriately adjusted to give the best viewing of the plot. The movie of the ECL waves from the square pattern is also attached in Supplementary Information (Movie S4).

## ECL formation mechanism of the F8BT/TPrAH System

F8BT is represented as R.

Tri-*n*-propylamine is represented as TPrAH.

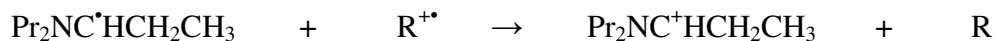
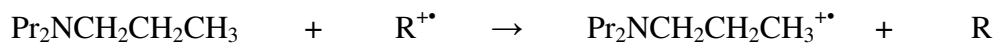
Oxidation reaction of F8BT



Oxidation reaction of TPrAH followed by a sequential deprotonation reaction



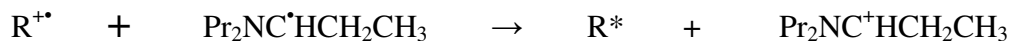
Neutralization of polymer radical cations ( $R^{+\bullet}$ ) by neutral TPrAH and  $TPrA^{\bullet}$



ECL could be formed by two schemes:

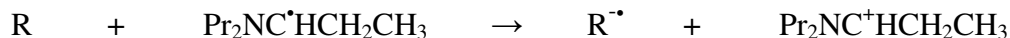
### Scheme 1.

Excited state of polymer is formed via electron transfer from TPrA radical ( $TPrA^{\bullet}$ ) to  $R^{+\bullet}$

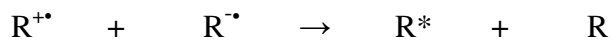


### Scheme 2.

First, neutral R is reduced by  $TPrA^{\bullet}$  by which polymer radical anions ( $R^{\bullet-}$ ) are formed.



Second, excited state of polymer ( $R^*$ ) is formed by annihilation of  $R^{+\bullet}$  and  $R^{\bullet-}$



## Methods summary

All materials and experimental apparatus in this work are the same as described in our previous publication<sup>3</sup> (except indicated otherwise). The ITO electrode was spin-coated with a 15–250-nm-thick F8BT layer only or embedded with isolated Au nanoparticles (diameter  $\sim 250$  nm,  $0.1$  particles/ $\mu\text{m}^2$ ) for the intentional scratches or well-defined nano-scale leaks experiments, respectively. The acetonitrile solution contained  $0.1$  M  $\text{LiClO}_4$  and  $0.1$  M TPA. The time dependence of the spatial ECL intensity was determined from a set of images that were recorded by a wide-field microscope (Nikon, Eclipse TE2000) and a CCD camera (Roper Scientific, Cascade 512B). The time ( $t$ ) labelled in each image represents the ending time of frame acquisition, e.g.  $t = 0.3$  s means the image was collected during  $0.2 \sim 0.3$  s after the application of the step potential with the integration time of  $0.1$  s. For the pulsed SMS-EC experiments, ECL images and current profiles were collected with the time-varying electrochemical potential,  $E(t)$ , applied to the ITO working electrode simultaneously.  $E(t)$  was maintained at the required potential relative to the QRE by a potentiostat (Autolab, PGSTAT 100). The reported potentials herein are relative to QRE. Potentials relative to a ferrocenium/ferrocene ( $\text{Fc}/\text{Fc}^+$ ) couple internal standard are about  $0.20 \pm 0.04$  V more negative than those of QRE. The F8BT films ( $50$  nm) with Au NPs embedded samples were prepared by spin-coating a  $150$   $\mu\text{L}$  of gold NP solution (BBInternational,  $250$  nm colloids in water) on the ITO followed by a  $150$   $\mu\text{L}$  of F8BT solution in toluene ( $14$  mg/mL).  $15$ ,  $50$  and  $250$  nm-thick of F8BT films were prepared by spin-coating a  $150$   $\mu\text{L}$  of F8BT solution in toluene ( $1.8$ ,  $14$  and  $28$  mg/mL, respectively) on the ITO. A spin rate of  $2000$  r.p.m. was used for  $60$  sec for all films. The films with scratches are made by an NSOM tip or AFM tip. No further treatment after the spin coating of F8BT film for the leak-free experiments. EC cell for the AFM measurement was an “open cell” including an Ag wire QRE and an Au foil (Alfa Aesar,  $25$   $\mu\text{m}$  thick) counter electrode immersed in the acetonitrile solution of  $0.05$  M  $\text{LiClO}_4$  and  $0.05$  M TPA and the F8BT film coated ITO working electrode. The AFM (Veeco, Dimension 3100) images were taken with a tapping mode (Veeco DNP tip, resonant frequency  $7.49$  KHz) and the tip was immersed in the solution. The film height change profile was recorded with the tip staying at a fixed

position (scan size: 1 nm×1 nm) while the potential sequence was applied and current was collected by a potentiostat simultaneously.

### Supporting ECL movies

Movie 1. ECL movie of “free wave” triggered by a Au-NP (~ 250 nm) embedded in a F8BT film (~ 50 nm) as shown in Fig. 1b.

Movie 2. ECL movie of “pinned wave” triggered by a Au-NP (~ 250 nm) embedded in a F8BT film (~ 50 nm) as shown in Fig. 1b.

Movie 3. ECL movie of waves triggered by Au-NPs (~ 250 nm) embedded in a F8BT film (~ 50 nm) demonstrates the waves propagation, collision and merging as showed in Fig. 1d. Image size is 287  $\mu\text{m}$   $\times$  287  $\mu\text{m}$ . Applied potential step is 1.8 V.

Movie 4. ECL movie of free waves triggered by a square-shaped scratch in a pure F8BT film (~ 250 nm) as shown in Figs. 2a-c.

### References

- (1) Palacios, R. E.; Fan, F. R. F.; Bard, A. J.; Barbara, P. F. *J. Am. Chem. Soc.* **2006**, *128*, 9028.
- (2) Palacios, R. E.; Fan, F. R. F.; Grey, J. K.; Suk, J.; Bard, A. J.; Barbara, P. F. *Nat. Mater.* **2007**, *6*, 680.
- (3) Chang, Y. L.; Palacios, R. E.; Fan, F. R. F.; Bard, A. J.; Barbara, P. F. *J. Am. Chem. Soc.* **2008**, *130*, 8906.