Supporting Information

Protonation-induced molecular permeation at oil/water Interface in electric field

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The research subject, a representative red ink molecule with single tertiary amine group [(E)-N-(5-(bis(2-ethylhexyl) amino)-2-((2-chloro-4-nitrophenyl) diazenyl) phenyl)-2-ethylhexanamide; RIM] was synthesized according to the following procedures (see Figure S1):

1. Synthesis of N-(3-(bis (2-ethylhexyl) amino) phenyl) acetamide

In brief, 3.16 g of N-acetyl-1,3-phenylenediamine (0.02 mol), 11.5 g of 1-bromo-iso-octane (0.06 mol) and 5.5 g of potassium carbonate (0.04 mol) were dissolved in 70 mL of N, N′-dimethylformamide (DMF) under the protection of nitrogen flow. After stirred for 9 h at 140 ℃, the reaction mixture was precipitated in 100 mL of ultrapure water and cooled to room temperature. These resulting precipitates was collected by extraction with ethyl acetate and vacuum concentration, and then further purified by column chromatography on silica gel. Finally, the pure N-(3-(bis (2-ethylhexyl) amino) phenyl) acetamide was obtained by the solvent removal. ^{1}H-nuclear magnetic resonance spectrum (NMR; 400MHz; deuterated chloroform, $CDCl_3$): 0.802 (12H, m), 3.122 (4H, m), 1.717 (2H, m), 1.183 (16H, m), 2.077 (3H, s), 7.282 (1H, s), 7.015 (1H, s), 6.536 (1H, s), 6.332 (1H, s).

2. Synthesis of N^1, N^1-bis (2-ethylhexyl) benzene-1, 3-diamine

7.84 g of N-(3-(bis (2-ethylhexyl) amino) phenyl) acetamide (0.02 mol) was dissolved in 200 mL of industrial alcohol, and then 16 mL of concentrated hydrochloric acid (HCl; 0.2 mol) was added dropwise. Subsequently, the mixture was stirred for 5 h at 80 ℃ under the protection of nitrogen flow. The reaction monitored using silica gel thin layer chromatography (TLC; ethyl acetate/ petroleum ether= 1/5) till fully completed. Finally, the mixture was neutralized with aqueous solution of sodium hydroxide, extracted with petroleum ether, and washed twice with ultrapure water. The pure product was obtained after the thorough removal of solvent.

3. Synthesis of N-(3-(bis (2-ethylhexyl) amino) phenyl)-2-ethylhexanamide

4 g of triethylamine (0.04 mol) was added to 200 mL of N, N-Dimethylformamide (DMF) solution containing 6.6 g of N^1, N^1-bis (2-ethylhexyl) benzene-1, 3-diamine (0.02 mol). Afterwards, 3.2 g of 2-ethylhexanoyl chloride (0.02 mol) was added dropwise. This mixture was stirred at room temperature for 1 h. The final product was

extracted with 100 mL of petroleum ether, followed by twice washing with ultrapure water and concentrating.

4. Synthesis of (E)-N-(5-(bis (2-ethylhexyl) amino)-2-((2-chloro-4-nitrophenyl) diazenyl) phenyl)-2-ethylhexanamide

1.72 g of 1-Chloro-2-nitrobenzene (0.01 mol) and 4.0 g of nitrosyl sulfuric acid (0.013 mol) were added into 10 mL of phosphoric acid and stirred for 2 h. And 4.58 g of N-(3-(bis (2-ethylhexyl) amino) phenyl)-2-ethylhexanamide (0.01 mol) was dissolved into 50 mL of industrial alcohol and cooled to 0~5 ℃. Both the two solutions was mixed for coupling. After 2 h, the reaction mixture was poured into 100 mL of ultrapure water. Subsequently, the crude product was extracted with ethyl acetate and then dried over anhydrous sodium sulfate. Finally, these product was further purified by filtration, concentration and column chromatography. ^{1}H-NMR (400 MHz; $CDCl_3$; see Figure S2): 12.567 (s, 1H); 8.319-8.314 (d, 2H); 8.109-8.104, 8.091-8.086 (dd, 1H); 7.801-7.785 (d, 1H); 7.692 (s, 1H); 6.509-6.504, 6.491-6.486 (dd, 1H); 3.401-3.286 (m, 4H); 2.347 (s, 1H); 1.801 (m, 2H); 1.651 (m, 2H); 1.501 (m, 2H); 1.230 (m, 20H); 0.847 (m, 18H).

5. Molecular structure characterization

All the ^{1}H-NMR spectra were measured on a Varian 400 MHz NMR system with Oxford NMR AS400 Magnet using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard.

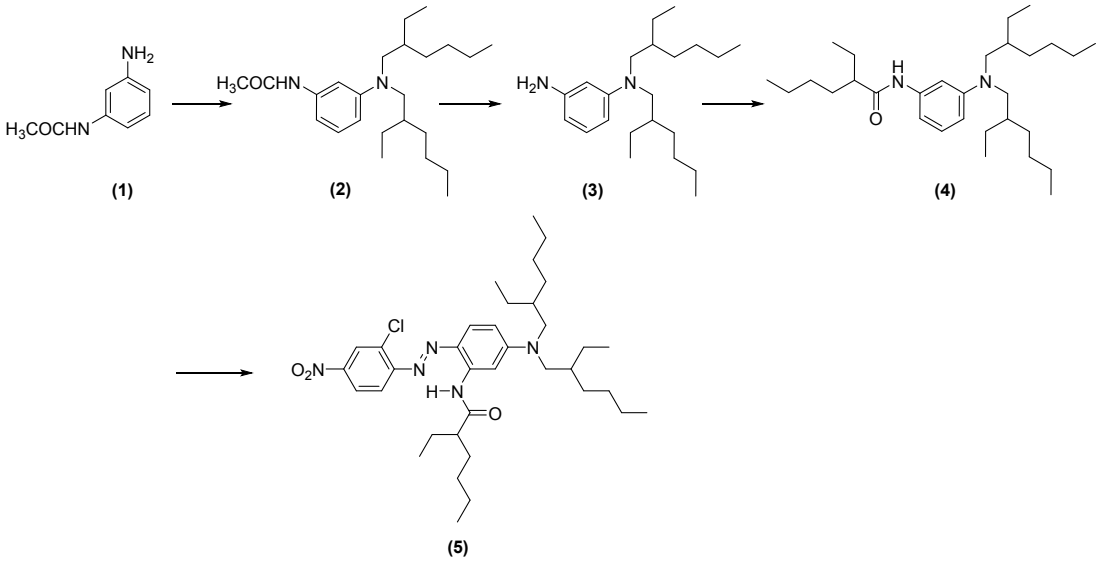

Figure S1. Synthesis route of N-(5-(bis (2-ethylhexyl) amino)-2-((2-chloro-4-nitrophenyl) diazenyl) phenyl)-2-ethylhexanamide (RIM).

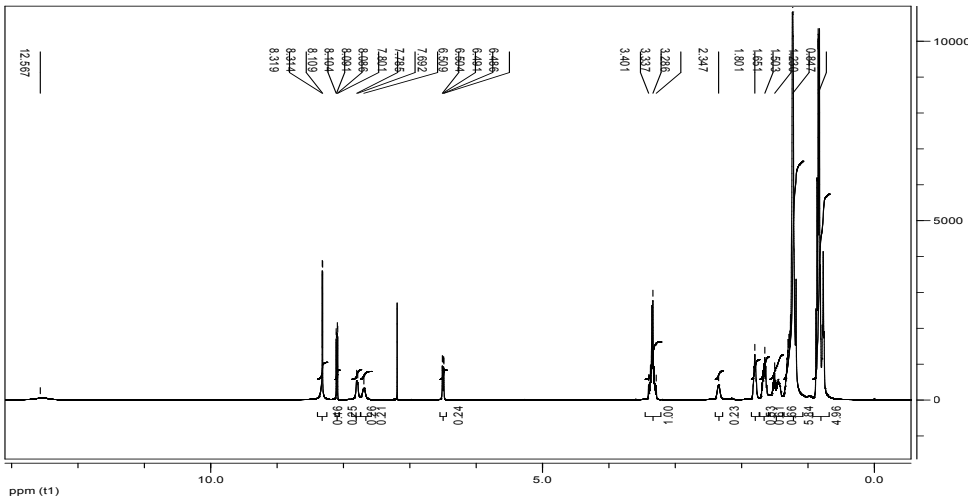

Figure S2. ^{1}H-NMR spectrum of (E)-N-(5-(bis (2-ethylhexyl) amino)-2-((2-chloro-4-nitrophenyl) diazenyl) phenyl)-2-ethylhexanamide (RIM).

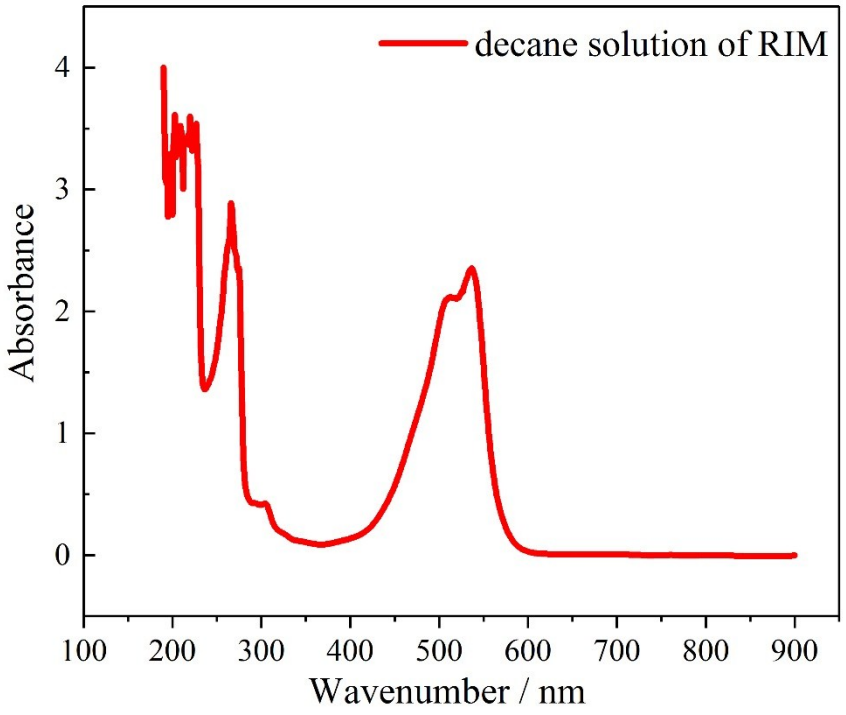

Figure S3. UV spectrophotometer of RIM's decane solution (2.5 wt.%).