

Support Information

Chemically functionalized conjugated oligoelectrolyte nanoparticles for enhancement of current generation in microbial fuel cells

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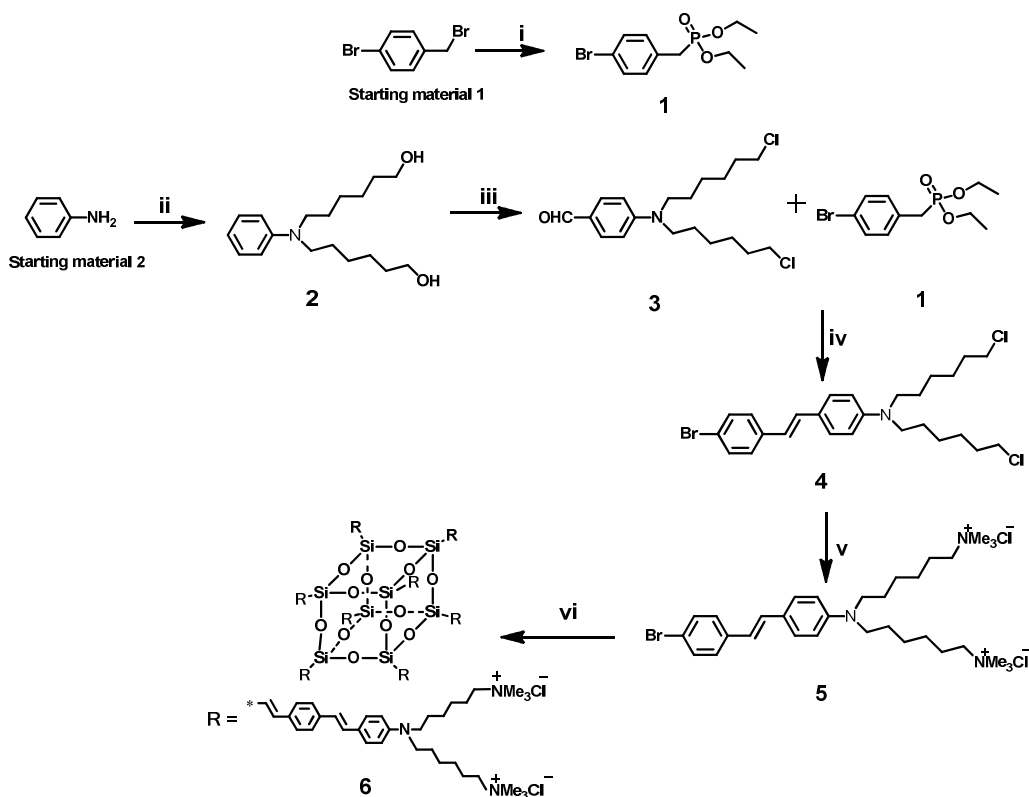
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Synthesis and characterization of COE NPs

Synthesis routes for the COE NPs. The reagents and conditions for the synthesis of COE NPs are as follows (Scheme S1):

- (i) Triethylphosphite/DCM, ZnBr₂, RT, 24h; (ii) 6-chloro-1-hexanol/n-butanol, K₂CO₃, reflux, 4 days; (iii) POCl₃/DMF, 100 °C, 2 h; (iv) t-BuOK in dry THF, room temperature, 8h; (v) NMe₃, THF/MeOH, 80 °C, 36 h; (vi) OvinPOSS in dry DMF, TEA, Pd(PPh₃)Cl₂, 100 °C, 36h.



Scheme S1 Synthesis routes for the synthesis of COE NPs.

Diethyl 4-bromobenzylphosphonate (**1**) and *N, N*-Bis(6'-iodohexyl)-4-aminobenzaldehyde (**3**) were synthesized according to the reported procedures and reported literature respectively.¹⁻²

Synthesis of (E)-4-(4-bromostyryl)-*N, N*-bis(6-chlorohexyl)aniline (4**).** A solution containing 16.3 mM of the phosphonate **1** and 13.5 mM of the aldehyde (**3**) was prepared in 30

mL dry THF. To the above mixture was added 13.5 mM of base potassium tert-butoxide. The resulting suspension was stirred over night at room temperature. The resulting mixture was diluted with chloromethane and washed with brine. The organic layer was dried over MgSO₄, and the volatile was evaporated. The crude product was purified by silica gel chromatography (dichloromethane/hexane=2:1) to afford 4 yield about 71% as a light yellow oil. ¹H NMR (400 MHz, CHCl₃-D, δ ppm): 7.41-7.49 (m, 2H), 7.31-7.37 (m, 4H), 6.98-7.02 (d, 1H), 6.78-6.82 (d, 1H), 6.60-6.62 (d, 2H), 3.53-3.56 (t, 4H), 3.27-3.31 (t, 4H), 1.76-1.83 (m, 4H), 1.57-1.65 (m, 4H), 1.45-1.53 (m, 4H), 1.32-1.40 (m, 4H). ¹³C NMR (100 MHz, CHCl₃-D, δ ppm): 147.83, 137.28, 131.58, 129.54, 127.90, 127.42, 124.35, 122.48, 119.99, 50.93, 45.01, 32.57, 27.20, 26.77, 26.44.

Synthesis of (E)-4-(4-bromostyryl)-N,N-bis(6'-(N,N,N-trimethylammonium)hexyl)aniline dichloride (5). In a round flask, 5 mL trimethylamine ethanol solution (31 wt%, 4.2 M) was added into a THF solution of (4) (2.2 g, 4.065 mM) under reflux at 80°C. Till the solution became dense and turbid, several drops of methanol was added to make the precipitate dissolved, another 2 mL trimethylamine ethanol solution was added to make (4) full quaternarization. After cooling, removed the solvent and excessive trimethylamine by reduced pressure distill, then the ultimate mixture was dropped into diethyl ether. Finally, some precipitate was obtained as a yellow solid. ¹H NMR (400 MHz, DMSO-D₆, δ ppm): 7.53-7.46 (m, 4H), 7.41-7.39 (d, 2H), 7.17-6.88 (m, 2H), 6.66-6.64 (d, 2H), 3.32-3.26 (m, 8H), 3.05 (s, 18H), 1.74-1.62 (m, 4H), 1.59-1.46 (m, 4H), 1.41-1.25 (m, 8H). ¹³C NMR (100MHz, DMSO-D₆, δ ppm): 148.09, 137.75, 131.93, 130.17, 128.44, 128.15, 124.11, 122.10, 119.58, 111.97, 65.69, 52.60, 50.38, 27.13, 26.41, 26.25, 22.55.

Synthesis of POSS based oligo(p-phenylene vinylene) electrolyte (COE NPs) (6). Octavinyl POSS (0.0348 g, 0.055 mmol), **(5)** (0.346 g, 0.55 mM), Pd(PPh₃)₂Cl₂ (19.3 mg, 27.5 μM) were placed in a 50 mL Schlenk flask under Ar atmosphere. A mixture of 5 mL dry DMF and 2.5 mL triethylamine (TEA) was then added to this flask. The mixture was vigorously stirred at 100 °C for 36 h. After cooling, it was filtered. The filtrate was poured into acetone to obtain some precipitate. The precipitate was collected and washed with acetone several times till supernatant was clear without **(5)** detected by UV absorbance. Finally, the product was purified by dialysis against Mill-Q water using a 3.5 KDa molecular weight cutoff dialysis membrane for 3 days. At last, an orange color solid was obtained. ¹H NMR (400 MHz, DMSO-D₆, δ ppm): 7.69-7.45 (m, 4H), 7.45-7.30 (m, 4H), 7.29-6.80 (m, 4H), 6.72-6.51 (d, 2H), 3.32-3.26 (m, 8H), 3.05 (s, 18H), 1.74-1.62 (m, 4H), 1.59-1.46 (m, 4H), 1.41-1.25 (m, 8H). ¹³C NMR (100MHz, DMSO-D₆, δ ppm): 147.95, 137.68, 135.91, 131.91, 130.17, 129.17, 127.22, 126.57, 124.47, 123.12, 123.05, 111.99, 65.70, 52.61, 50.41, 27.15, 26.41, 26.23, 22.56.

The ¹H NMR spectra of the OPVE showed a singlet in the region 3.05 ppm corresponding to 18 protons, revealing a high degree of quaternarization of the OPVE (Figure S 1-1). The peak of the COE NPs in the region 7.2-7.3 ppm was assigned to the proton from Octavinyl POSS (Figure S 1-2). The integrated area between the peak at ppm 6.64 to 7.56 and 3.06 ppm (the alkyl protons from the NMe₃ units) suggested that nearly all vinyl bonds of vinyl were substituted by cationic oligofluorene. In compared with the ¹³C NMR spectrum of the OPVE (Figure S 2-1), the peaks at 119.58 ppm disappeared and the peaks at 136 ppm and 129 ppm appeared (Figure S 2-2), further confirming the successful coupling reaction between POSS and OPVE.

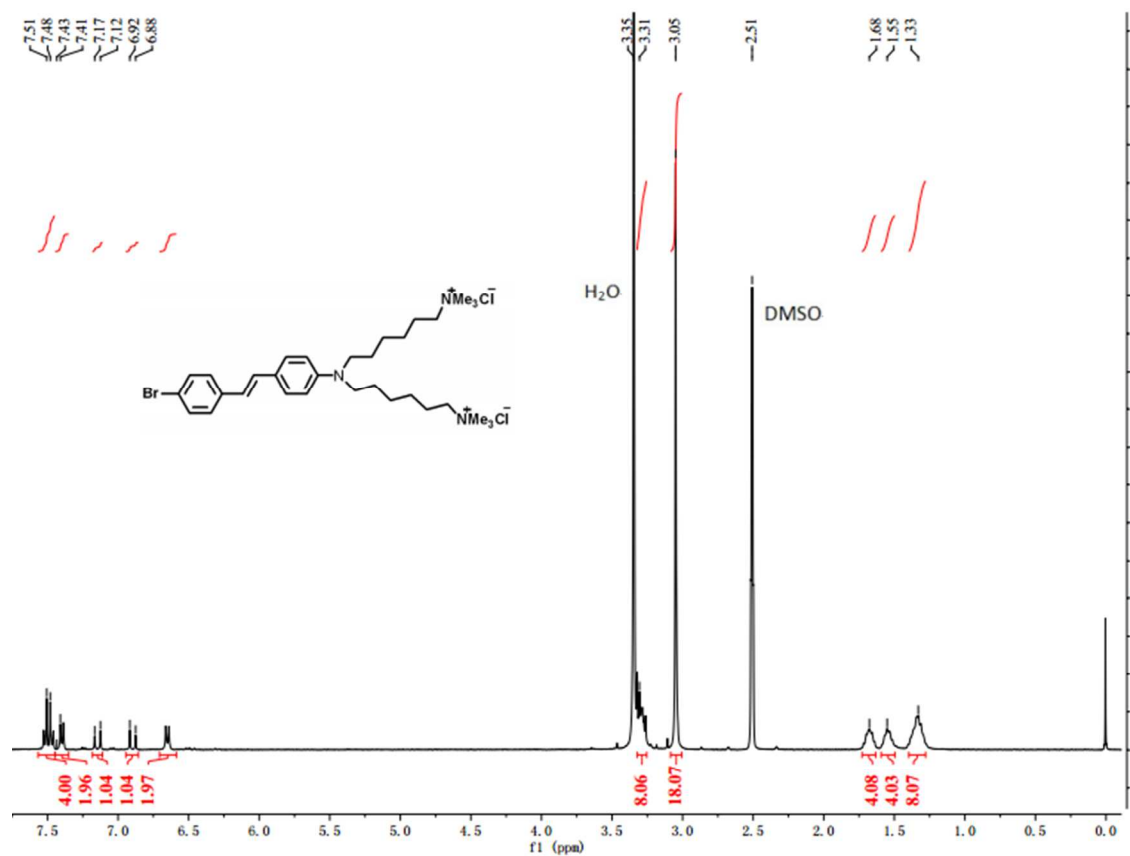


Figure S1-1 ¹H NMR of the precursor of COE NPs – OPVE.

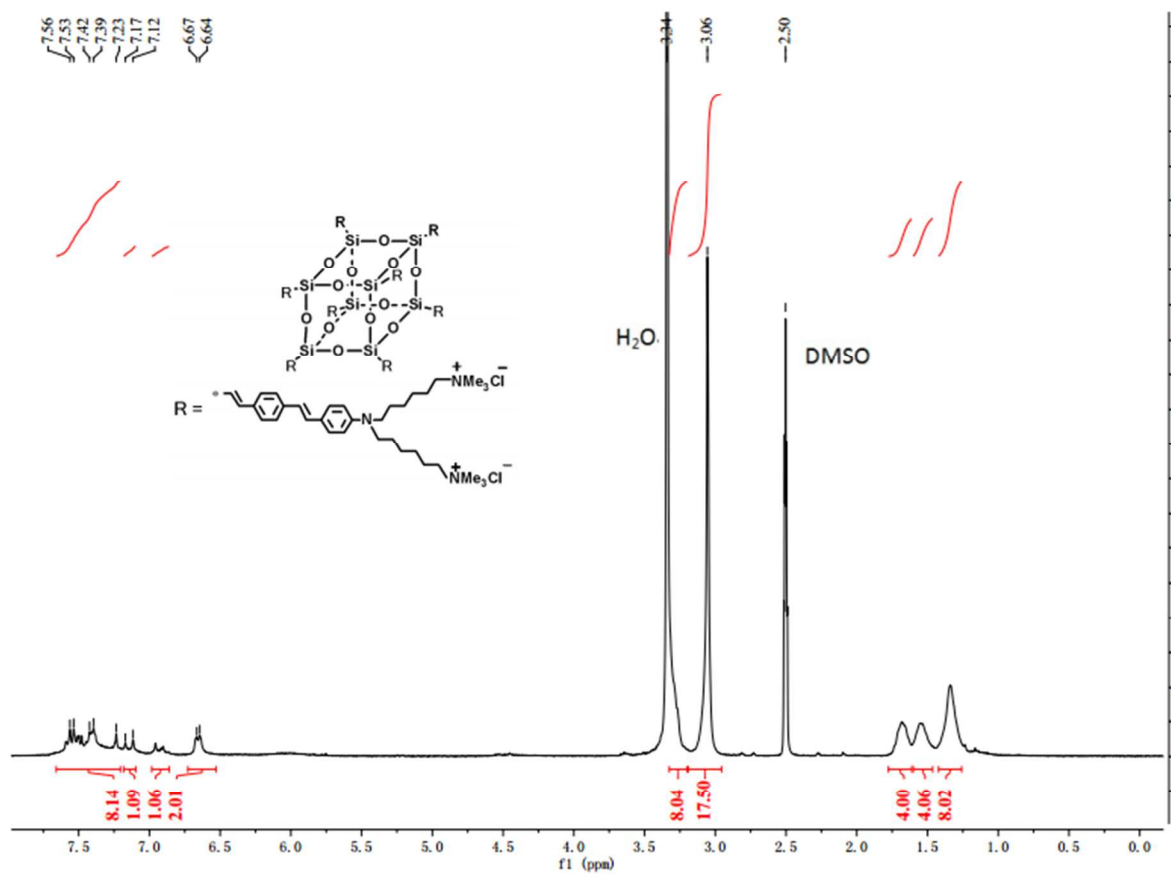


Figure S1-2 ^1H NMR of COE NPs.

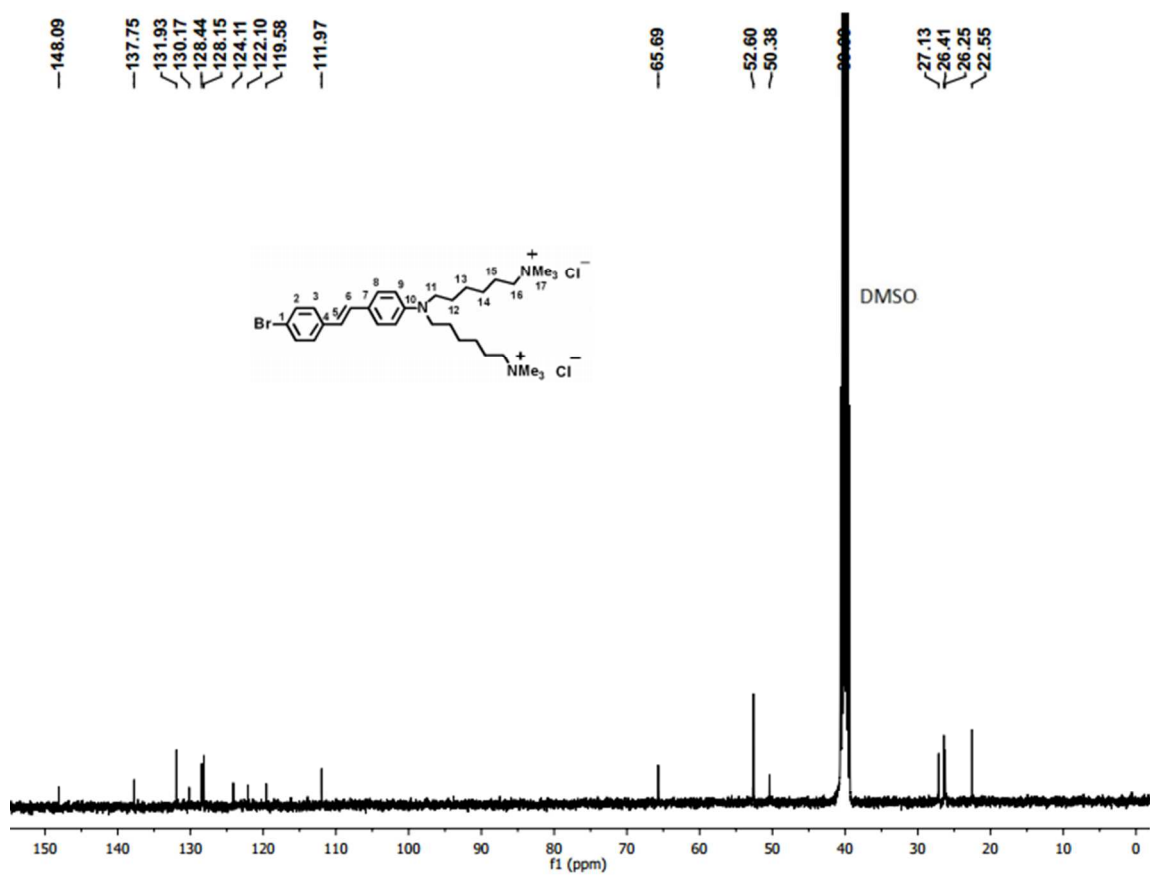


Figure S2-1 ^{13}C NMR of the precursor of COE NPs – OPVE.

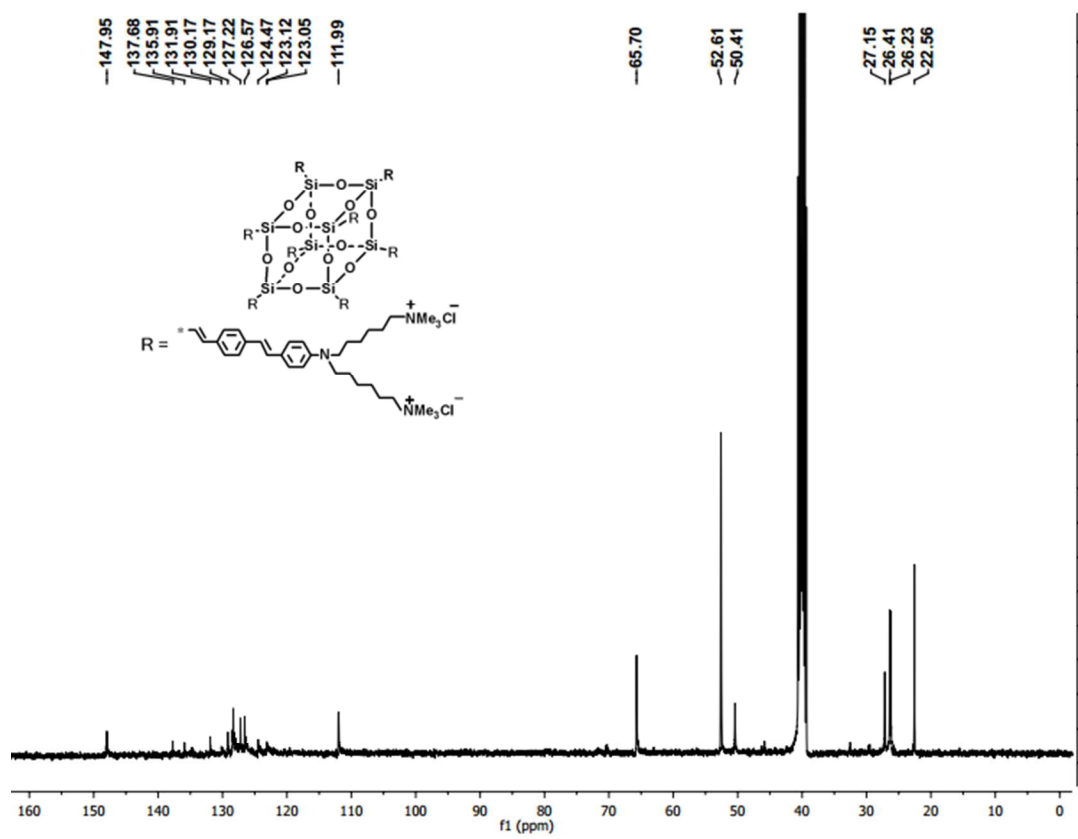


Figure S2-2 ^{13}C NMR of COE NPs.

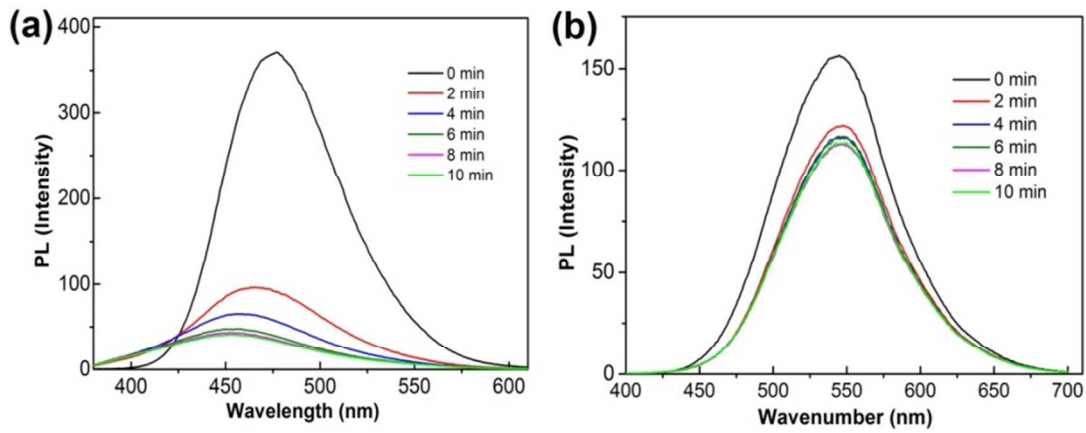


Figure S3 The fluorescent photostability contrast between (a) precursor OPVE (100 μM) and (b) COE NPs (12.5 μM) under UV light.

REFERENCE

- (1). Rajeshwaran, G. G.; Nandakumar, M.; Sureshbabu, R.; Mohanakrishnan, A. K., Lewis Acid-Mediated Michaelis– Arbuzov Reaction at Room Temperature: A Facile Preparation of Arylmethyl/Heteroarylmethyl Phosphonates. *Organic Lett.* **2011**, *13* (6), 1270-1273.
- (2). Woo, H. Y.; Liu, B.; Kohler, B.; Korystov, D.; Mikhailovsky, A.; Bazan, G. C., Solvent effects on the two-photon absorption of distyrylbenzene chromophores. *J. Am. Chem. Soc.* **2005**, *127* (42), 14721-14729.