Electronic Supplementary Information (ESI)

Pyrene-imidazolium complexed graphene for the selective fluorescent detection of G-quadruplex capable DNA

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Experimental section

Instruments: ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 apparatus. IR spectra were obtained for KBr pellets, over the range 400 – 4000 cm^{-1}, with a Shimadzu FT-IR 8400S instrument, and mass spectra were obtained by a JEOL JMS-700 mass spectrometer. The optical absorption spectra of the samples were obtained using a UV–vis spectrophotometer (Hitachi U-2900).

SEM observations: The specimens were examined with a JEOL JEM-2010 transmission electron microscope operating at 200 kV using an accelerating voltage of 100 kV and a 16 mm working distance. Scanning electron micrographs of the samples were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG). The SEM accelerating voltage was 5–15 kV and the emission current was 10 μA.

Compound 2: The suspension of 1-pyrenemethanol **3** (2 g, 8.6 mmol) in toluene (100 mL) was cooled to 0 °C followed by addition of phosphorus tribromide (1 mL, 10.5 mmol) via syringe. The mixture was stirred at 0 °C for 1 h and then warmed to room temperature, during which the reaction became homogeneous. Saturated Na_2CO_3 solution 50 mL was added slowly and the reaction was stirred until it cooled to room temperature. The phases were separated, and the organic phase was washed with H_2O (50 mL X 2), brine (50 mL X 2) and dried over Mg_2SO_4. The yellow filtrate was concentrated to minimum volume. The yellow needle-like solid was collected and dried. The mother liquid was concentrated again and repeated the crystallization process. The total product was 2.3 g in 91% yield. m.p.: 136 °C ^{1}H-NMR ($CDCl_3$, 250MHz) d 5.23 (s, 2H), 8.02 (m, 5H), 8.21 (m, 3H), 8.35 (d, J = 9.3 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 62.5 MHz) d 32.28, 122.80, 124.58, 124.84, 125.07, 125.61, 126.26, 127.32, 127.67, 128.01, 128.22, 129.03, 130.51, 130.73, 131.17, 131.92.

Compound PI: A solution of 1-bromomethylpyrene **2** (0.66 g, 2.24 mmol) and bisimidazole **1** (0.15 g, 1 mmol) in 160 mL acetonitrile was refluxed for 24 h under argon. After cooling to

the room temperature, the precipitate was filtered and washed with ether. The bromide salt (694 mg, 93%) was dissolved in 25 mL DMF. (During the dropwise addition of saturated aqueous KPF_6 solution, precipitate was formed. After washing the precipitate several times with water, desired product was obtained as a white solid (663 mg, 81%). ^{1}H-NMR (DMSO, 250 MHz) (for bromide salt) d 6.31 (s, 4H), 6.58 (s, 2H), 8.02 (s, 2H), 8.03 (s, 2H), 8.08e8.52 (m, 18 H), 9.51 (s, 2H). ^{13}C-NMR (DMSO, 62.5 MHz) d 50.39, 58.29, 122.36, 123.53, 123.56, 124.04, 125.17, 125.83, 125.93, 126.06, 126.54, 126.71, 127.19, 128.29, 128.72, 128.84, 130.06, 130.61, 131.61, 137.62.; HRMS (FAB) calcd for $C_{41}H_{30}F_6N_4P$ $[M\text{-}PF_6]^+$ 723.2101, found 723.2111.

Preparation of reduced graphene oxide (r-GO): Graphene oxide was prepared from natural graphite (Sigma-Aldrich) using a modified Hummers' method. In a typical reaction, 1.00 g of graphite, 1.00 g of $NaNO_3$, and 50 mL of H_2SO_4were stirred in an ice bath for 30 min. Following, 8.00 g of $KMnO_4$ was slowly added. The solution was transferred to a 35 °C water bath and stirred for about 2 h to form a thick green paste. After that, the mixture was stirred for 3 days at room temperature. Then, 80 mL of water was added very slowly followed by stirring for 1 h while the temperature was increased to ~90 °C. Finally, 200 mL of water was added followed by the slow addition of 20 mL of H_2O_2 (30%), turning the color of the solution from dark brown to a pale brown yellowish. The warm solution was then filtered and washed with water. GO solution (~0.2wt%) was ultrasonicated for 1 h, and the remaining non-exfoliated GO was removed by centrifugation at 14000 rpm (20817 rcf) for 30 min. The solution was then membrane filtered. The final product was then stored under vacuum for drying.

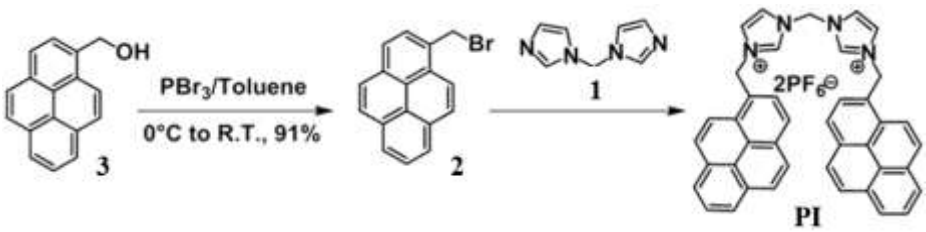
Preparation of SiO_2 nanoparticles: A solution of 9.5 mol L^{-1} H_2O and 0.9 mol L^{-1} ammonia was prepared in 200 mL EtOH and heated to 40 °C under N_2 atmosphere. TEOS was then added up to 0.25 mol L^{-1} overall concentration with vigorous stirring. Stirring was continued for 30 min. At the end of the reaction, SiO_2 nanoparticles were collected by centrifugation at 10000 rpm for 10 min at 20 °C and then washed with water and EtOH for several times and separated. The final product was obtained after drying for 12 h under reduced pressure at room temperature.

Preparation of APTES-modified SiO_2 nanoparticles: The obtained silica templates (0.5 g)

were further dispersed into 50 mL of dry toluene solution via sonication. After 30 min, 0.5 mL of (3-aminopropyl)triethoxysilane (APTES) was poured into the above solution and refluxed for 24 h under argon atmosphere to obtain APTES-modified silica nanotemplates.

Reduced graphene oxide encapsulated SiO_2 nanoparticles: r-GO encapsulated SiO_2 was fabricated via the electrostatic interaction between positively charged APTES-modified SiO_2 and negatively charged r-GO in aqueous solutions. In a typical process, 20 mL of APTES-modified SiO_2 dispersion (0.5 mg mL^{-1}) was added into a 30 mL aqueous r-GO suspension (0.05 mg mL^{-1}) under mild magnetic stirring. After 1 h, 0.5 mL of hydrazine (35 wt%) was added into the above suspension to r-GO. The solution was membrane filtered and washed with water.

Preparation of XG_3, X_2G_2, XG_2: Oligonucleotides were purchased from Bionics and dissolved in 10 mM phosphate buffer, containing 100 mM NaCl, 0.1 mM EDTA, pH 7.0. This buffer solution was used during the whole fluorescent experiments. The compound (1 mM) stock in CH_3CN was prepared and the final test samples were made up in 1% CH_3CN and 99% buffer solution. For all measurements, excitation was at 343 nm. The excitation slit width was 5 nm. Fluorescence emission spectra were obtained using RF-5301/PC Spectrofluorophotometer (Shimadzu).



Full DNA Sequence for 30-mer and 50-mer dsDNA:

30-mer dsDNA having 6 repeats of guanosine trimer (G3) motifs present per DNA duplex

5’-TTGGGTGGGTATGGGTGGGTATGGGTGGGT-3’

50-mer dsDNA having 10 repeats of guanosine trimer (G3) motifs present per DNA duplex

5’-TTGGGTGGGTATGGGTGGGTATGGGTGGGTATGGGTGGGTATGGGTGGGT-3’

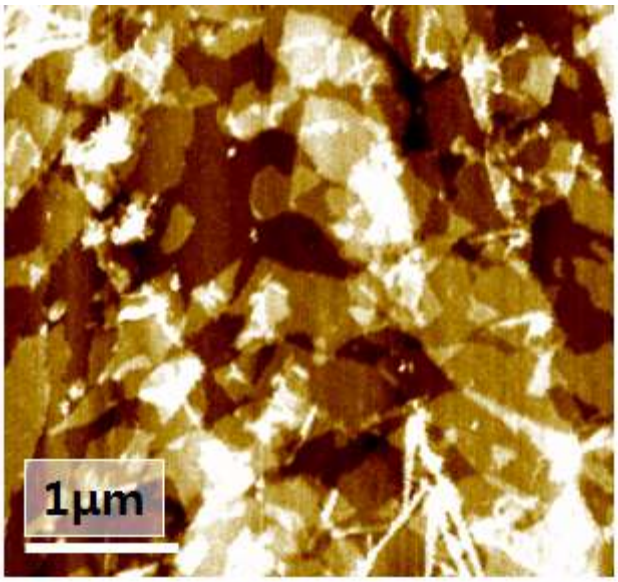


Fig. S1 AFM image of grapheme oxide sheets.

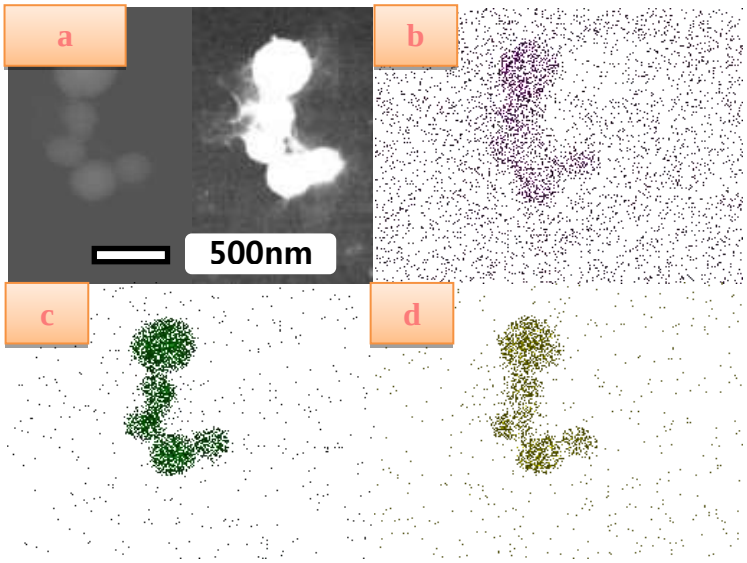


Fig. S2 TEM mapping images (a) bright-field image, (b) Si mapping, (c) O mapping and (d) C mapping of SiO_2@rGO-**PI**.

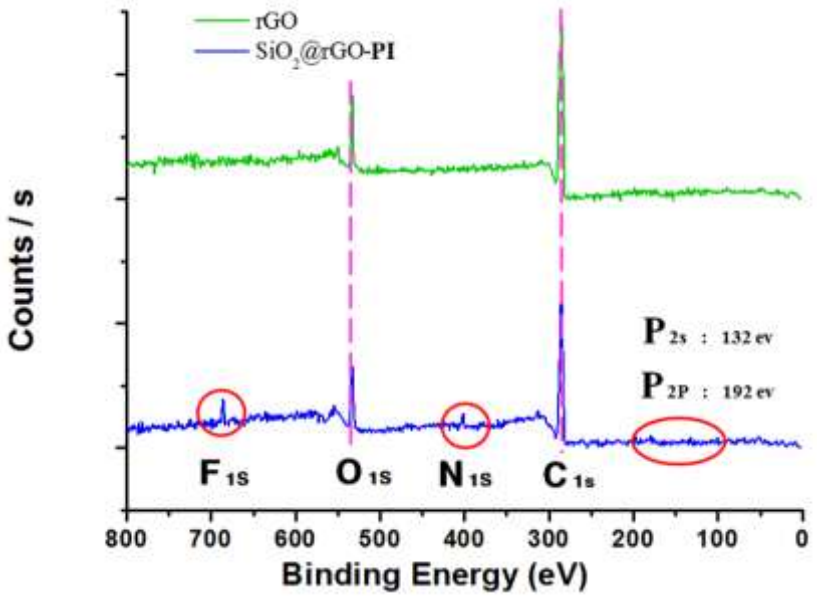


Fig. S3 XPS data for rGO (green) and SiO_2@rGO exposed to **PI** (blue) which shows the presence of F1s and N1s peaks owing to the capture of **PI** on the SiO_2@rGO surface.

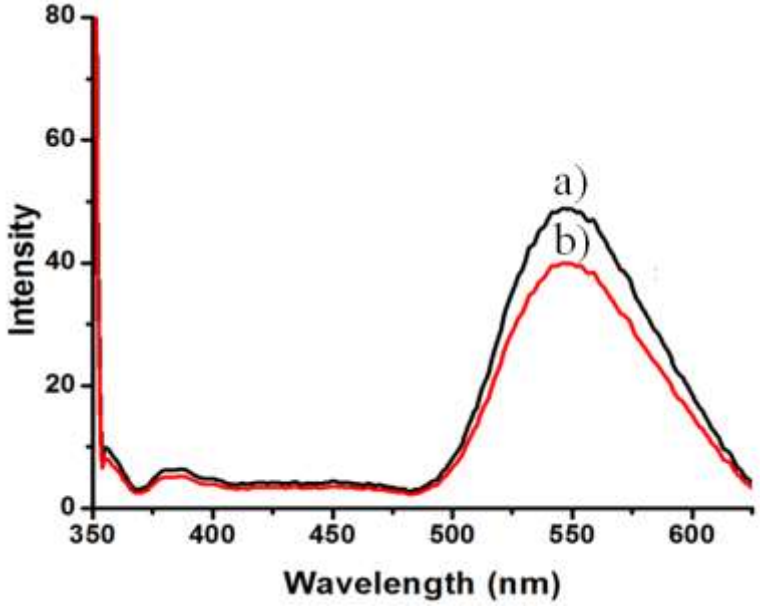


Fig. S4 Fluorescence spectra of **PI** by addition of (a) 30-mer (10 nM) and (b) 50-mer (6.0 nM) dsDNA in the presence of SiO_2@rGO-**PI**.