Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplemental Information

Enhance of an efficient sensitivity for the diclhovors detection by a low-weighted gelator based bolaamphiphile amino acid derivatives decorated with a hybrid graphene quantum dots/enzyme hydrogel

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29 pages

1. Synthesis procedure of gelators

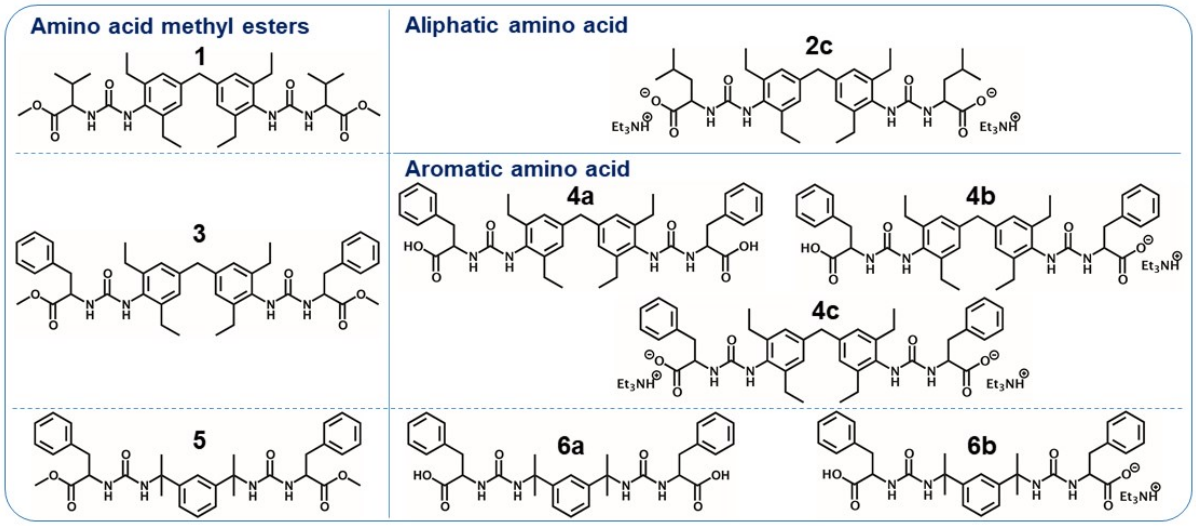
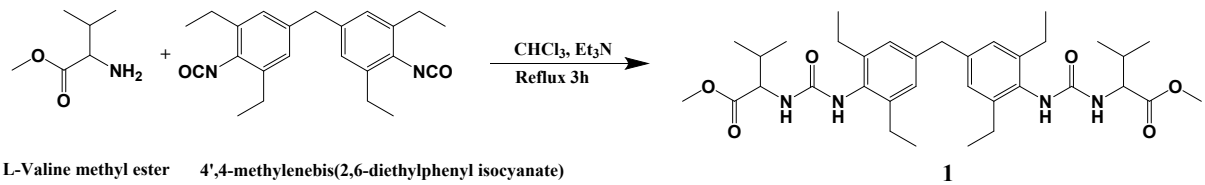


Figure S1. Molecular structures of gelators **1-6b** based on bis(urea) and amino acid derivatives.

1.1 Compound 1



L-Valine methyl ester 4',4-methylenebis(2,6-diethylphenyl isocyanate) **1**

Figure S2. Synthetic pathway of compound **1**

Triethylamine (0.78 ml, 5.59 mmol) was added to a suspension of L-valine methyl ester (0.44 g, 3.37 mmol) in $CHCl_3$ (15 ml). 4,4'-methylenebis(2,6-diethylphenyl isocyanate) (0.59 g, 1.63 mmol) was dissolved in $CHCl_3$ (15 ml) and slowly added to the mixture. The combined solution was stirred under reflux at 68 ^oC for 3 h. 20 ml of water was added and. the solution was extracted with $CHCl_3$ (4x50 ml). The organic phase was dried over $MgSO_4$, and the solvent was removed under vacuum. The solid was recrystallized from 20:30 ml of acetone: hexane. The product was isolated by filtration and washed with cold $CHCl_3$ to afford compound **1** as a white solid (0.653 g, 1.04 mmol, 64 % yield) mol. wt. = 624.81. **^{1}H NMR** (400 MHz, DMSO-d6) δ 7.46 (s, 2H, N<u>H</u>), 6.93 (s, 4H, Ar<u>H</u>), 6.54 (s, 2H, N<u>H</u>), 4.14 (q, ^3J= 4 Hz, NHC<u>H</u>), 3.81(s, 2H, ArC<u>H$_2$</u>Ar), 3.65 (s, 6H, OC<u>H$_3$</u>), 2.47 (q, ^3J= 4 Hz, 8H, ArC<u>H$_2$</u>CH$_3$), 1.07 (t, ^3J= 8 Hz, 12H, ArCH$_2$C<u>H$_3$</u>), 0.90 (d, ^3J= 12 Hz, 12H, CHC<u>H$_3$</u>); **^{13}C{^{1}H} NMR** (400 MHz, DMSO-d6) δ 173.46 (<u>C</u>O$_2$CH$_3$), 156.90 (C=O), 142.20 (Ar<u>C</u>), 126.66 (Ar<u>C</u>), 58.18 (<u>C</u>H), 52.09 (<u>C</u>H), 30.95 (<u>C</u>H$_2$), 24.90 (<u>C</u>H$_2$), 19.46 (<u>C</u>H$_3$), 18.25 (<u>C</u>H$_3$), 15.16 (<u>C</u>H$_3$); **ESI-MS** (*m/z*): 648.64 m/z $[M+Na]^+$ (calc. 647.36 m/z), 625.19 m/z $[M+H]^+$ (calc. 625.38 m/z); Elemental **analysis calc.** for $C_{35}H_{52}N_4O_6$: C 67.28, H 8.39, N 8.97%; found: C 67.46, H 8.46, N 8.87%.

1.2 Compound 2c

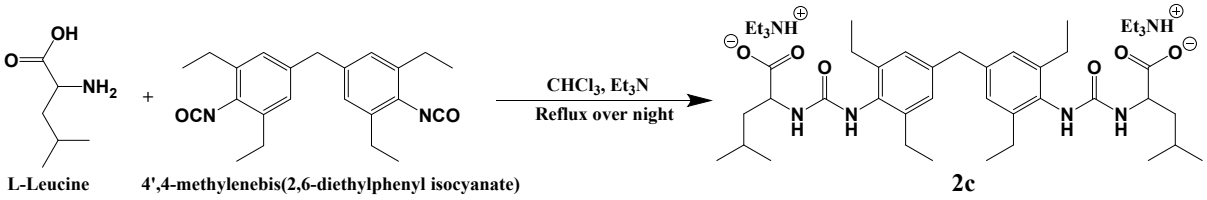


Figure S3. Synthetic pathway of compound **2c**

Triethylamine (0.78 ml, 5.59 mmol) was added to a suspension of L-leucine (0.428 g, 3.27 mmol) in EtOH:$CHCl_3$ (1:15 ml). 4,4'-methylenebis(2,6-diethylphenyl isocyanate) (0.59 g, 1.63 mmol) was dissolved in $CHCl_3$ (15 ml) and slowly added to the mixture. The combined solution was stirred under reflux at 68 ^oC for overnight. 20 mL of water was added and the solution was extracted using CH_3Cl (4x50 ml). The organic phase was dried over $MgSO_4$ and the solvent was removed under vacuum. The solid was recrystallized from 20:30 ml of acetone: hexane over 3h. The product was isolated by filtration and washed with cold $CHCl_3$ (40 ml) to afford compound **2c** as a light-yellow solid (0.643 g, 0.77 mmol, 48 % yield) mol. wt. = 827.19. **^{1}H NMR** (400 MHz, DMSO-d6) δ 7.77 (s, 2H, N<u>H</u>), 6.93 (s, 4H, Ar<u>H</u>), 6.31 (s, 2H, N<u>H</u>), 4.06

(q, ^3J= 8.0 Hz, 2H, $CH_2C\underline{H}NH$), 3.81 (s, 2H, $ArC\underline{H}_2Ar$), 2.56 (m, 12H, $NC\underline{H}_2CH_3$), 2.46 (m, 8H, $ArC\underline{H}_2CH_3$), 1.71 (m, 2H, $C\underline{H}(CH_3)_2$), 1.47 (m, 4H, $C\underline{H}_2CH$), 1.09 (t, 18H $NCH_2C\underline{H}_3$), 0.88 (d, ^3J= 8.0 Hz, 12H , $CHC\underline{H}_3$) **ESI-MS** (*m/z*): 625.39 m/z $[M\text{-}2Et_3N+H]^+$ (calc. 625.39 m/z), $[M+H]^+$ (calc. 827.63 m/z); Elemental **analysis calc.** for $C_{47}H_{82}N_6O_6$: C 68.24, H 9.99, N 10.16%; found: C 64.43, H 9.06, N 9.18%. The compound was found to strongly retain $CHCl_3$ **calc.** for $C_{47}H_{82}N_6O_6 \cdot 0.5CHCl_3$: C 64.32, H 9.38, N 9.48%.

1.3 Compound 3

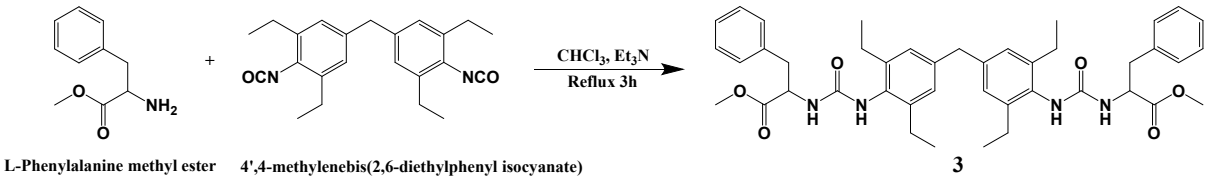


Figure S4. Synthetic pathway of compound **3**

Triethylamine (0.78 ml, 5.59 mmol) was added to a suspension of L-phenylalanine methyl ester (0.60 g, 3.37 mmol) in $CHCl_3$ (15 ml). 4,4'-methylenebis(2,6-diethylphenyl isocyanate) (0.59 g, 1.63 mmol) was dissolved in $CHCl_3$ (15 ml) and slowly added to the mixture. The combined solution was stirred under reflux at 68 ^oC for 3 h. The product was isolated by filtration washed with cold $CHCl_3$ to afford compound **3** a white solid (0.871 g, 1.21 mmol, 74 % yield) mol. wt. = 720.90. **^{1}H NMR** (400 MHz, DMSO-d6) δ 7.57 (s, 2H, N$\underline{H}$), 7.30 (m, 10H, Ar$\underline{H}$), 6.91 (s, 4H, Ar$\underline{H}$), 6.76 (s, 2H, N$\underline{H}$), 4.47 (q, ^3J= 8.0 Hz, 2H, $CH_2C\underline{H}NH$), 3.80 (s, 2H, $ArC\underline{H}_2Ar$), 3.62 (s, 6H, $OC\underline{H}_3$), 3.04 (dd, ^3J= 8.0 Hz, 2H, $CHC\underline{H}_xH_yAr$), 2.98 (dd, ^3J= 8.0 Hz, 2H, $CHCH_x\underline{H}_yAr$), 2.42 (q, ^3J= 8.0 Hz, 8H, $ArC\underline{H}_2CH_3$), 1.04 (t, ^3J= 8.0, 12H, $ArCH_2C\underline{H}_3$); **^{13}C{^{1}H} NMR** (400 MHz, DMSO-d6) δ 173.20 ($\underline{C}O_2CH_3$), 156.46 (C=O), 137.55 (Ar$\underline{C}$), 129.65 (Ar$\underline{C}$), 128.67 (Ar$\underline{C}$), 126.97 (Ar$\underline{C}$), 126.63 (Ar$\underline{C}$), 52.19 ($\underline{C}H$), 24.83 ($\underline{C}H_2$), 15.13 ($\underline{C}H_3$); **ESI-MS** (*m/z*): 721.67 m/z $[M+Na]^+$ (calc. 721.38 m/z); Elemental **analysis calc.** for $C_{43}H_{52}N_4O_6$: C 71.64, H 7.27, N 7.74%; found: C 71.39, H 7.32, N 7.80%.

1.4 Compound 4a

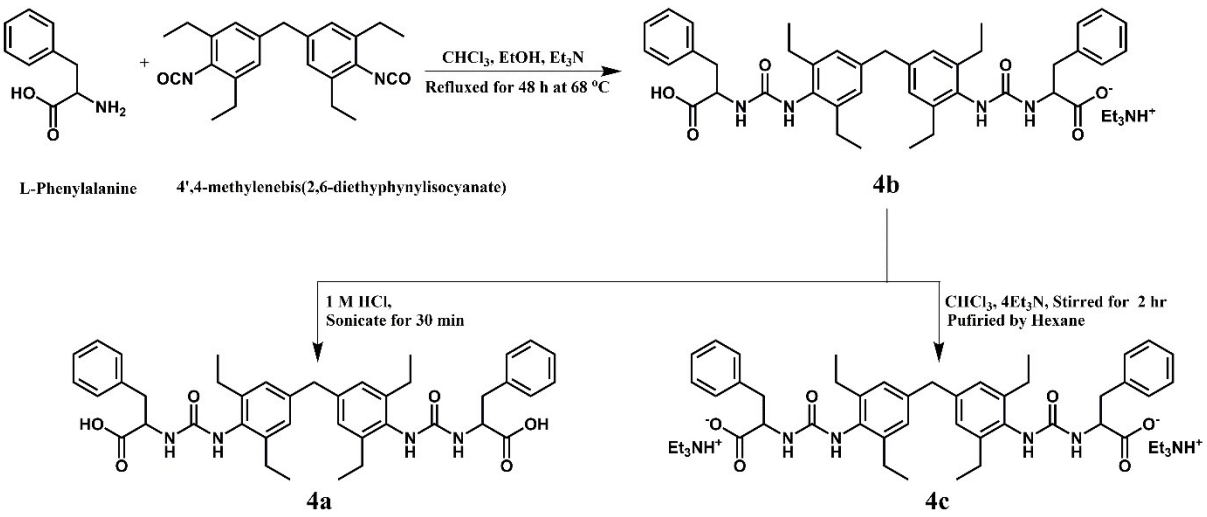


Figure S5. Synthetic pathway route to gelators **4b, 4a a**nd **4c** respectively.

Compound **4a** was synthesized using the same method as **4b (see below)**, followed by suspoension in 1 M aqueous HCl (250 ml), and sonication for 30 minutes. The product was isolated by filtration and washed with water and cold $CHCl_3$ to afford compound **4a** as a light-yellow solid. (0.448 g, 0.65 mmol, 40 % yield) mol. wt. = 692.84. **^{1}H NMR** (400 MHz, DMSO-d6) δ 12.67 (s, 1H, OH), 7.53 (s, 2H, NH), 7.24 (m, 10H, ArH), 6.91 (s, 4H, ArH), 6.34 (s, 2H, NH), 4.44 (q, ^3J= 8.0 Hz, 2H, CH_2CHNH), 3.82 (s, 2H, $ArCH_2Ar$), 3.08-2.93 (m, 4H, $CHCH_2Ar$), 2.40 (q, ^3J= 8.0 Hz, 8H, $ArCH_2CH_3$), 1.09 (t, ^3J= 8.0 Hz, 12H, $ArCH_2CH_3$); **^{13}C{^{1}H} NMR** (400 MHz, DMSO-d6) δ 174.08 (CO_2H), 156.43 (C=O), 142.21 (ArC), 137.77 (ArC), 129.74 (ArC), 128.54 (ArC), 126.84 (ArC), 54.16 (CH), 41.14 (CH_2), 38.06 (CH_2), 24.80 (CH_{3x}), 15.12 (CH_{3y}); **ESI-MS** (*m/z*): 693.60 m/z $[M+H]^+$ (calc. 693.36 m/z); Elemental **analysis calc.** for $C_{41}H_{48}N_4O_6$: C 71.08, H 6.98, N 8.09%; found: C 69.66, H 7.00, N 7.88%. The compound was found to strongly retain HCl **calc.** for $C_{41}H_{48}N_4O_6 \cdot 0.3HCl$: C 69.97, H 6.92, N 7.96%.

1.5 Compound 4b

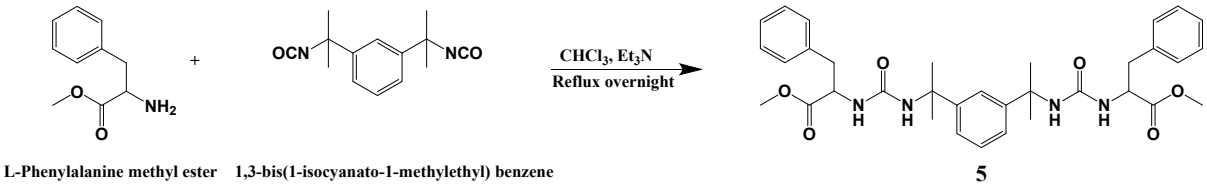
Triethylamine (0.78 ml, 5.59 mmol) was added to a suspension of L-phenylalanine (0.54 g, 3.27 mmol) in EtOH:$CHCl_3$ (1:15 ml). 4,4'-methylenebis(2,6-diethylphenyl isocyanate) (0.59 g, 1.63 mmol) was dissolved in $CHCl_3$ (15 ml) was slowly added to the mixture. The combined solution was stirred under reflux at 68 ^oC for 48 h. 20 ml of water was added and the solution was extracted with $CHCl_3$ (4x50 ml). The organic phase was dried over $MgSO_4$ and the solvent was removed under vacuum. The solid was recrystallized from 20:30 ml of acetone: hexane over 3h. The product was isolated by filtration and washed with cold $CHCl_3$ (40 ml) to afford compound **4b** as a light-yellow solid (0.995 g, 1.25 mmol, 77 % yield) mol. wt. = 794.03. **^{1}H NMR** (400 MHz, DMSO-d6) δ 7.59 (s, 2H, NH), 7.23 (m, 10H, ArH), 6.90 (s, 4H, ArH), 6.28 (s, 2H, NH), 4.27 (q, ^3J= 8 Hz, 2H, CH_2CHNH), 3.80 (s, 2H, $ArCH_2Ar$), 3.04-2.96 (m, 4H, $CHCH_2Ar$), 2.76 (q, ^3J= 8 Hz, 6H, NCH_2CH_3), 2.45 (q, ^3J= 4 Hz, 8H, $ArCH_2CH_3$), 1.05 (t, ^3J= 8 Hz, 9H and 12H , NCH_2CH_3 and $ArCH_2CH_3$); **^{13}C{^{1}H} NMR** (400 MHz, DMSO-d6) δ 174.19 (CO_2H), 156.41 (C=O), 142.26 (ArC), 138.46 (ArC), 129.94 (ArC), 128.28 (ArC), 126.49 (ArC), 54.49 (CH), 45.76 (NCH_2CH_3), 41.15 (CH_2), 38.23 (CH_2), 24.85 (CH_{3x}), 15.14 (CH_{3y}), 10.34 (NCH_2CH_3); **ESI-MS** (*m/z*): 693.59 m/z $[M\text{-}Et_3N+H]^+$ (calc. 693.36 m/z); **Elemental analysis calc.** for $C_{47}H_{63}N_5O_6$: C 71.09, H 8.00, N 8.82%; found: C 66.62, H 7.59, N 8.17%. The compound was found to strongly retain $CHCl_3$ **calc.** for $C_{47}H_{63}N_5O_6 \cdot 0.5CHCl_3$: C 66.83, H 7.50, N 8.20%. The residual $CHCl_3$ can be observed by **^{1}H NMR** at δ 8.27 (s).

1.6 Compound 4c

Compound **4b** (0.25 g, 0.35 mmol) was suspended in 10 ml $CHCl_3$. Triethylamine (0.19 ml, 1.41 mmol) was added, the solution was stirred for 2 h at room temperature and the solvent was then evaporated under vacuum to yield a yellow oil. Hexane (25ml) was added and the mixture sonicated for 1 minute to induce crystallisation. The product was isolated by filtration and washed with hexane to yield compound **4c** as a light-yellow solid. (0.208 g, 0.23 mmol, 66 % yield) mol. wt. = 894.60. **^{1}H NMR** (400 MHz, DMSO-d6) δ 7.60 (s, 2H, NH), 7.19 (m, 10H, ArH), 6.90 (s, 4H, ArH), 6.29 (s, 2H, NH), 4.24 (q, ^3J= 8 Hz, 2H, CH_2CHNH), 3.80 (s, 2H, $ArCH_2Ar$), 3.08-2.93 (m, 4H, $CHCH_2Ar$), 2.70 (q, ^3J= 8 Hz, 12H, NCH_2CH_3), 2.45 (q, ^3J= 8 Hz, 8H, $ArCH_2CH_3$), 1.05 (t, ^3J= 8 Hz, 19H and 12H , NCH_2CH_3 and $ArCH_2CH_3$); **ESI-MS**

(*m/z*): 715.52 m/z $[M\text{-}2Et_3N+Na]^+$ (calc. 715.35 m/z), 693.55 m/z $[M\text{-}2Et_3N+H]^+$ (calc. 693.36 m/z); Elemental **analysis calc.** for $C_{53}H_{78}N_6O_6$: C 71.11, H 8.78, N 9.39%; found: C 65.20, H 8.90, N 8.21%. The compound was found to strongly retain $CHCl_3$ and hexane **calc.** for $C_{53}H_{78}N_6O_6 \cdot 0.85CHCl_3 \cdot 0.5$Hexane: C 65.54, H 8.50, N 8.07%. The residual $CHCl_3$ and hexane can be observed by **^{1}H NMR** at δ 8.34 (s) and δ 1.25 (m).

1.7 Compound 5



L-Phenylalanine methyl ester 1,3-bis(1-isocyanato-1-methylethyl) benzene **5**

Figure S6. Synthetic pathway of compound **5**

Triethylamine (0.78 ml, 5.59 mmol) was added to a suspension of L-phenylalanine methyl ester (0.70 g, 3.27 mmol) in $CHCl_3$ (15 ml). 1,3-Bis(1-isocyanato-1-methylethyl)benzene (0.38 ml, 1.63 mmol) was dissolved in $CHCl_3$ (15 ml) and slowly added to the mixture. The combined solution was stirred under reflux at 68 ^oC for overnight. The solvent was removed under vacuum, and 20 ml of acetone was then added, followed by 30 ml of hexane. The solid was collected by filtration, washed with water, suspended in 1 M aqueous HCl (250 ml), and then sonicated for 30 minutes. The product was isolated by filtration and washed with water to afford compound **5** as a white solid (0.415 g, 0.689 mmol, 42 % yield) mol. wt. = 602.72. **^{1}H NMR** (400 MHz, DMSO-d6) δ 7.03-7.35 (m, 14H, Ar<u>H</u>), 6.51 (s, 2H, N<u>H</u>), 6.16 (d, ^3J= 8.0 Hz, 2H, N<u>H</u>), 4.35 (q, ^3J= 8.0 Hz, 2H, $CH_2C\underline{H}NH$), 3.59 (s, 6H, $OC\underline{H}_3$), 2.97-2.79 (m, 4H, $CHC\underline{H}_x\underline{H}_yAr$), 1.47 (s, 12H, $CC\underline{H}_3$); **^{13}C{^{1}H} NMR** (400 MHz, DMSO-d6) δ 173.51 ($\underline{C}O_2CH_3$), 156.77 (C=O), 148.55 (Ar<u>C</u>), 137.43 (Ar<u>C</u>), 129.62 (Ar<u>C</u>), 128.73 (Ar<u>C</u>), 127.66 (Ar<u>C</u>), 127.02 (Ar<u>C</u>), 122.72 (Ar<u>C</u>), 121.70 (Ar<u>C</u>), 54.87 ($\underline{C}CH_3$), 54.11 (<u>C</u>H), 52.09 ($\underline{C}H_2$), 38.23 ($\underline{C}H_3$), 30.68 ($\underline{C}H_3$), 30.47 ($\underline{C}H_3$); **ESI-MS** (*m/z*): 625.49 m/z $[M+Na]^+$ (calc. 625.29 m/z), 603.55 m/z $[M+H]^+$ (calc. 603.31 m/z); Elemental **analysis calc.** for $C_{34}H_{42}N_4O_6$: C 67.75, H 7.02, N 9.30%; found: C 67.23, H 7.04, N 9.22%.

1.8 Compound 6a

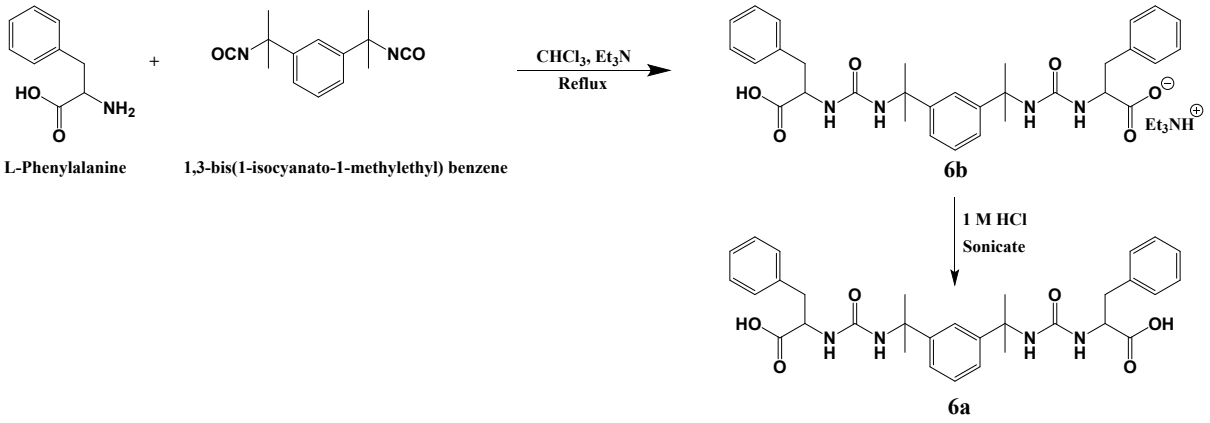


Figure S7. Synthetic pathway route to gelators **6b** and **6a** respectively.

Compound **6b (see below)** was suspended in 1 M aqueous HCl (250 ml), and sonicated for 30 min. The product was isolated by filtration and washed with water and cold $CHCl_3$ to yield compound **6a** as a white solid. (0.594 g, 1.03 mmol, 63 % yield) mol. wt. = 574.28. **^{1}H NMR** (400 MHz, DMSO-d6) δ 12.57 (s, 2H, O<u>H</u>) 7.47-7.04 (m, 14H, Ar<u>H</u>), 6.51 (s, 2H, N<u>H</u>), 6.04 (d, ^3J= 8 Hz, 2H, N<u>H</u>), 4.31 (q, ^3J= 8 Hz, 2H, $CH_2C\underline{H}NH$), 2.98 (dd, ^3J= 4 Hz, 2H, $C\underline{H}_xH_yAr$), 2.85 (dd, ^3J= 4 Hz, 2H, $CH_x\underline{H}_yAr$), 1.47 (d, ^3J= 4 Hz, 12H, $ArCH_2C\underline{H}_3$); **^{13}C{^{1}H} NMR** (400 MHz, DMSO-d6) δ 174.35 ($\underline{C}O_2H$), 156.85 (C=O), 148.64 (Ar<u>C</u>), 137.81 (Ar<u>C</u>), 129.71 (Ar<u>C</u>), 128.59 (Ar<u>C</u>), 127.60 (Ar<u>C</u>), 126.84 (Ar<u>C</u>), 122.71 (Ar<u>C</u>), 121.71 (Ar<u>C</u>), 54.81 ($\underline{C}CH_3$), 53.87 ($\underline{C}H$), 38.24 ($\underline{C}H_2$), 30.69 ($\underline{C}H_{3x}$), 30.56 ($\underline{C}H_{3y}$); **ESI-MS** (*m/z*): 575.48 m/z $[M+H]^+$ (calc. 575.28 m/z), 597.49 m/z $[M+Na]^+$ (calc. 597.49 m/z); Elemental **analysis calc.** for $C_{32}H_{38}N_4O_6$: C 66.88, H 6.67, N 9.75%; found: C 66.50, H 6.83, N 9.64%.

1.9 Compound 6b

Triethylamine (0.78 ml, 5.59 mmol) was added to a suspension of L-phenylalanine (0.54 g, 3.27 mmol) in EtOH:$CHCl_3$ (1:15 ml). 1,3-Bis(1-isocyanato-1-methylethyl)benzene (0.38 ml, 1.63 mmol) was dissolved in $CHCl_3$ (15 ml) and slowly added to the mixture. The combined solution was stirred under reflux at 68 ^{o}C for 48 h. 20 ml of water was added and the solution extracted with $CHCl_3$ (4x50 ml). The organic layers were combined and the solvent removed under vacuum. The solid was recrystallized from 20:30 ml of acetone: hexane over 3h, the product was isolated by filtration and washed with cold $CHCl_3$ (40 ml) to afford compound **6b** as a white solid (0.921g, 1.36 mmol, 84 % yield) mol. wt. = 675.40. **^{1}H NMR** (400 MHz,

DMSO-d6) δ 7.33-7.06, (m, 14H, ArH), 6.55 (s, 1H, a-NH), 6.50 (s, 1H, b-NH), 6.19 (m, 1H, a-NH), 6.01 (d, ^3J= 4.0 Hz, 1H, b-NH), 4.22 (q, ^3J= 8.0 Hz, 2H, CH_2CHNH), 3.90 (m, 1H, $CH_3CH_2NH^+$), 2.87-2.95 (m, 4H, $CHCH_xH_yAr$), 2.76 (q, ^3J= 8 Hz, 6H, $CH_3CH_2NH^+$), 1.49 (d, ^3J= 4.0 Hz 6H, CCH_{3x}), 1.46 (d, ^3J= 8.0 Hz 6H, CCH_y), 1.05 (t, 9H, ^3J= 8.0 Hz, $CH_3CH_2NH^+$); **^{13}C{^{1}H} NMR** (400 MHz, DMSO-d6) δ 174.88 (a-CO_2^-), 174.46 (b-CO_2H), 157.17 (a-C=O), 156.88 (b-C=O), 148.81 (ArC), 138.48 (a-ArC), 138.23 (b-ArC), 129.82 (a-ArC), 129.72 (b-ArC), 128.45 (a-ArC), 128.43, 127.66 (a-ArC), 127.58(b-ArC), 126.63 (a-ArC), 126.54(b-ArC), 122.84 (a-ArC), 122.68(b-ArC), 122.54 (a-ArC), 121.70 (b-ArC), 54.93 (a-CCH_3), 54.83 (b-CCH_3), 54.70 (a-CH), 54.63 (b-CH), 45.78 (NCH_2CH_3), 38.47 (a-CH_2), 38.39 (b-CH_2), 31.40 (a-CH_{3x}), 31.14 b-CH_{3x}), 30.86 (a-CH_{3y}), 30.80 (b-CH_{3y}), 10.36 (NCH_2CH_3); **ESI-MS** (*m/z*): 575.56 m/z $[M\text{-}Et_3N+H]^+$ (calc. 575.28 m/z), 597.49 m/z $[M\text{-}Et_3N+Na]^+$ (calc. 597.49 m/z); Elemental **analysis calc.** for $C_{38}H_{53}N_5O_6$: C 67.53, H 7.90, N 10.36%; found: C 65.77, H 7.72, N 9.74%. The compound was found to strongly retain $CHCl_3$ **calc.** for $C_{47}H_{82}N_6O_6{\cdot}0.2CHCl_3$: C 64.32, H 9.38, N 9.48%. The residual $CHCl_3$ can be observed by **^{1}H NMR** at δ 8.34 (s).

2. NMR spectra

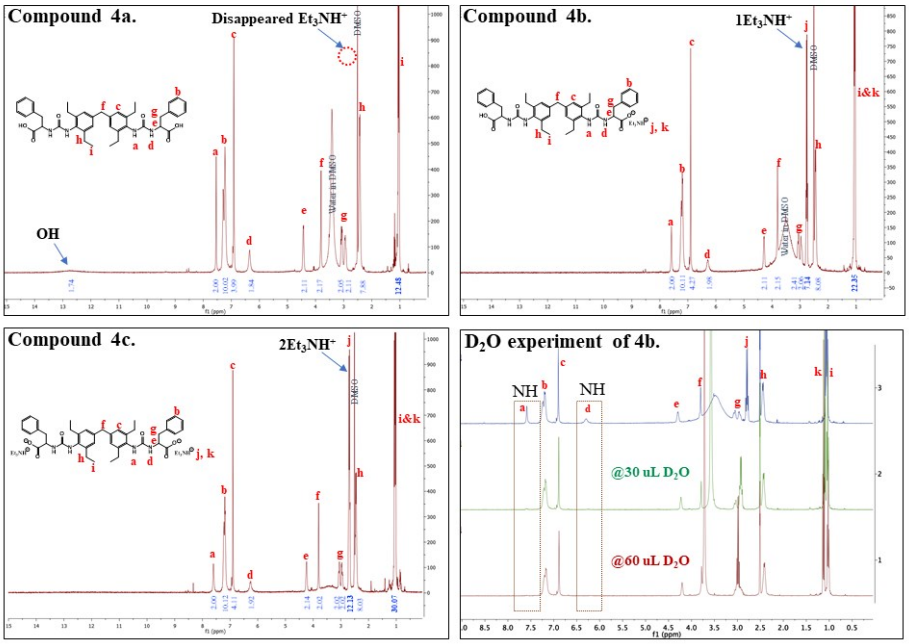


Figure S8. NMR spectra of compounds **4a-4c** and D_2O exchange experiment of compound **4b**.

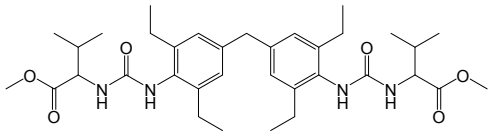
3. Gel formation studies

The gelation behavior of each gelator was examined in several solvents with different polarities including water, ethanol (EtOH), methanol (MeOH), 1-propanol, acetone, dimethyl sulfoxide (DMSO), chloroform, hexane, cyclohexane and cyclohexanone. 0.5 mL of each solvent was added to 5 mg (1% wt) of each gelator in a sealed vial. The mixture was sonicated for 30 sec, and then heated for 30 seconds. Gel formation was identified by the inversion test [1].

Table S1. Gel formation studies of compound **1**.

Compound	**%**	**Solvent**	**GQDs** (mg/ml)	**Time**							**comment**
				1 min	**5 min**	**30 min**	**4 h**	**24 h**	**48 h**	**7 days**	
1	1.0	Water	-	I	I	I	I	I	I	I	
1	1.0	EtOH	-	S	P	P	P	P	G	G	
1	1.0	MeOH	-	S	P	P	P	P	P	P	
1	1.0	1-Propanol	-	S	P	P	P	P	P	G	
1	1.0	Acetone	-	S	G	G	G	G	G	G	
1	1.0	DMSO	-	S	S	S	S	P	P	P	
1	1.0	Chloroform	-	S	P	P	P	P	P	P	
1	1.0	Hexane	-	I	I	I	I	I	P	P	
1	1.0	Cyclohexane	-	I	I	I	I	I	P	P	
1	1.0	Cyclohexanone	-	S	G	G	G	G	G	G	
1	1.0	10% EtOH/Water	-	P	P	P	P	P	P	P	
1	1.0	20% EtOH/Water	-	P	P	P	P	P	P	P	
1	1.0	50% EtOH/Water	-	S	P	P	P	P	P	P	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



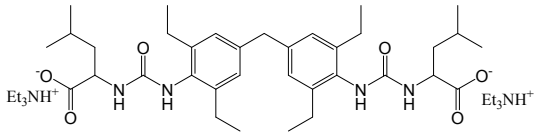
Compound **1.**

Compound **1** can form gels in acetone and cyclohexanone but it is insoluble in water and mixtures of ethanol/water.

Table S2. Gel formation studies of compound **2c**.

Compound	%	Solvent	GQDs (mg/ml)	Time							comment
				1 min	5 min	30 min	4 h	24 h	48 h	7 days	
2c	1.0	Water	-	I	I	I	I	I	I	I	
2c	1.0	EtOH	-	I	I	I	I	I	I	I	
2c	1.0	MeOH	-	I	I	I	I	I	I	I	
2c	1.0	1-Propanol	-	P	P	P	P	P	P	P	
2c	1.0	Acetone	-	I	I	I	I	I	I	I	
2c	1.0	DMSO	-	S	S	P	P	P	P	P	
2c	1.0	Chloroform	-	P	P	P	P	P	P	P	
2c	1.0	Hexane	-	I	I	I	I	I	I	I	
2c	1.0	Cyclohexane	-	P	P	P	P	P	P	P	
2c	1.0	Cyclohexanone	-	S	S	S	S	S	S	S	
2c	1.0	10% EtOH/Water	-	I	I	I	I	I	I	P	
2c	1.0	20% EtOH/Water	-	I	I	I	I	I	I	P	
2c	1.0	50% EtOH/Water	-	S	P	P	P	P	P	P	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



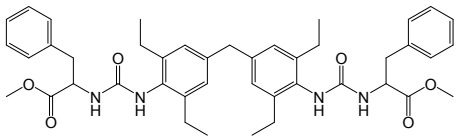
Compound **2c.**

Compound **2c** cannot form gels in any solvents.

Table S3. Gel formation studies of compound **3**.

Compound	%	Solvent	GQDs (mg/ml)	Time							comment
				1 min	5 min	30 min	4 h	24 h	48 h	7 days	
3	1.0	Water	-	I	I	I	I	I	I	I	
3	1.0	EtOH	-	G	G	G	G	G	G	G	
3	1.0	MeOH	-	G	G	G	G	G	G	G	
3	1.0	1-Propanol	-	G	G	G	G	G	G	G	
3	1.0	Acetone	-	G	G	G	G	G	G	G	
3	1.0	DMSO	-	S	S	S	S	S	S	S	
3	1.0	Chloroform	-	S	S	S	S	PG	G	G	
3	1.0	Hexane	-	P	P	P	P	P	P	P	
3	1.0	Cyclohexane	-	P	P	P	P	P	P	P	
3	1.0	Cyclohexanone	-	S	G	G	G	G	G	G	
3	1.0	10% EtOH/Water	-	I	P	P	P	P	P	P	
3	1.0	20% EtOH/Water	-	P	P	P	P	P	P	P	
3	1.0	50% EtOH/Water	-	P	P	P	P	P	P	G	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



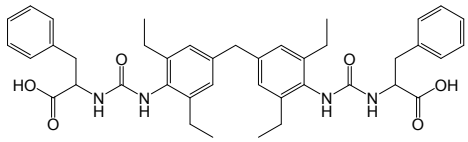
Compound **3.**

Compound **3** can form gels in ethanol, methanol, propanol, acetone and cyclohexanone but is insoluble in water and mixtures of 10 or 20% ethanol/water.

Table S4. Gel formation studies of compound **4a**.

Compound	**%**	**Solvent**	**GQDs** (mg/ml)	**Time**							**comment**
				1 min	**5 min**	**30 min**	**4 h**	**24 h**	**48 h**	**7 days**	
4a	1.0	Water	-	I	I	I	I	I	I	I	
4a	1.0	EtOH	-	S	P	P	P	P	P	P	
4a	1.0	MeOH	-	S	P	P	P	P	P	P	
4a	1.0	1-Propanol	-	S	P	P	G	G	G	G	
4a	1.0	Acetone	-	P	G	G	G	G	G	G	
4a	1.0	DMSO	-	S	S	S	S	S	S	S	
4a	1.0	Chloroform	-	P	P	P	P	P	P	P	
4a	1.0	Hexane	-	P	P	P	P	P	P	P	
4a	1.0	Cyclohexane	-	P	P	P	P	P	P	P	
4a	1.0	Cyclohexanone	-	S	G	G	G	G	G	G	
4a	1.0	10% EtOH/Water	-	P	P	P	P	P	P	P	
4a	1.0	20% EtOH/Water	-	P	P	P	P	P	P	P	
4a	1.0	50% EtOH/Water	-	S	G	G	G	G	G	G	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



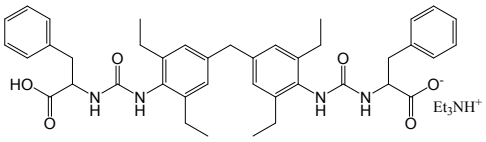
Compound **4a**

Compound **4a** can form gels in 1-propanol, acetone and cyclohexanone but is insoluble in water and the behavior tends towards gelation in mixtures of ethanol/water, especially in 50% EtOH/Water

Table S5. Gel formation studies of compound **4b**.

Compound	%	Solvent	GQDs (mg/ml)	Time							comment
				1 min	5 min	30 min	4 h	24 h	48 h	7 days	
4b	1.0	Water	-	S	PG	PG	PG	PG	PG	PG	
4b	1.0	EtOH	-	S	P	P	P	P	P	P	
4b	1.0	MeOH	-	P	P	P	P	P	PG	PG	
4b	1.0	1-Propanol	-	S	P	P	P	P	P	P	
4b	1.0	Acetone	-	P	P	P	P	P	P	P	
4b	1.0	DMSO	-	S	S	S	S	S	S	S	
4b	1.0	Chloroform	-	S	PG	PG	G	G	G	G	
4b	1.0	Hexane	-	I	I	I	I	I	I	I	
4b	1.0	Cyclohexane	-	I	I	P	P	P	P	P	
4b	1.0	Cyclohexanone	-	S	G	G	G	G	G	G	
4b	1.0	10% EtOH/Water	-	S	S	S	S	PG	PG	PG	
4b	1.0	20% EtOH/Water	-	G	G	G	G	G	G	G	
4b	1.0	50% EtOH/Water	-	G	G	G	G	G	G	G	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



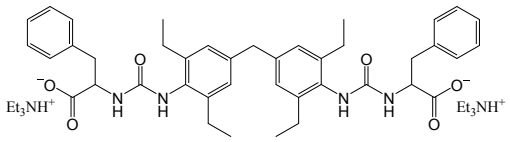
Compound **4b**

Compound **4b** can form gels in chloroform and cyclohexanone. It showed partial gelation of water and the behavior tended towards gelation in the mixture of ethanol/water, especially in 20 and 50% EtOH/water.

Table S6. Gel formation studies of compound **4**c

Compound	%	Solvent	GQDs (mg/ml)	Time							comment
				1 min	5 min	30 min	4 h	24 h	48 h	7 days	
4c	1.0	Water	-	S	S	S	S	PG	PG	PG	Clear PG
4c	1.0	EtOH	-	S	S	S	S	P	P	P	
4c	1.0	MeOH	-	S	S	S	S	P	P	P	
4c	1.0	1-Propanol	-	S	S	S	S	P	P	P	
4c	1.0	Acetone	-	S	G	G	G	G	G	G	Opaque gel
4c	1.0	DMSO	-	S	S	S	S	S	S	S	
4c	1.0	Chloroform	-	S	G	G	G	G	G	G	
4c	1.0	Hexane	-	I	I	P	P	P	P	P	
4c	1.0	Cyclohexane	-	I	I	P	P	P	P	P	
4c	1.0	Cyclohexanone	-	S	G	G	G	G	G	G	
4c	1.0	10% EtOH/Water	-	S	S	S	S	PG	PG	G	
4c	1.0	20% EtOH/Water	-	S	S	S	S	PG	PG	G	
4c	1.0	50% EtOH/Water	-	S	S	S	S	P	P	P	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



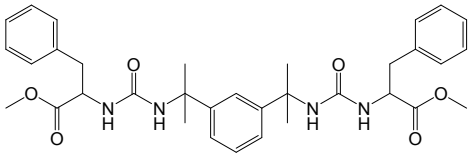
Compound **4c**

Compound **4c** can form gels in acetone, chloroform and cyclohexanone. It showed partial gelation of water and was the behavior tended towards gelation in mixtures of ethanol/water. Surprisingly, 1% of gelator **4c** can form a partial gel in water.

Table S7. Gel formation studies of compound **5**.

Compound	**%**	**Solvent**	**GQDs**	**Time**							**comment**
			(mg/ml)	**1 min**	**5 min**	**30 min**	**4 h**	**24 h**	**48 h**	**7 days**	
5	1.0	Water	-	I	I	I	I	I	I	I	
5	1.0	EtOH	-	S	S	S	S	S	S	S	
5	1.0	MeOH	-	S	S	S	S	S	S	S	
5	1.0	1-Propanol	-	S	S	S	S	S	S	S	
5	1.0	Acetone	-	S	S	S	S	S	S	S	
5	1.0	DMSO	-	S	S	S	S	S	S	S	
5	1.0	Chloroform	-	S	S	S	S	S	S	S	
5	1.0	Hexane	-	P	P	P	P	P	P	P	
5	1.0	Cyclohexane	-	P	P	P	P	P	P	P	
5	1.0	Cyclohexanone	-	S	S	S	S	S	S	S	
5	1.0	10% EtOH/Water	-	S	I	I	I	I	I	I	
5	1.0	20% EtOH/Water	-	S	I	I	I	I	I	I	
5	1.0	50% EtOH/Water	-	S	S	S	S	S	S	P	Small crystal

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



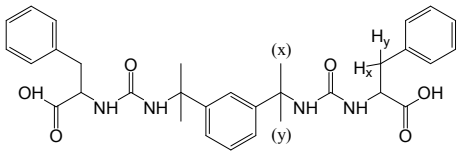
Compound **5**.

Compound **5** cannot form a gel in any solvents.

Table S8. Gel formation studies of compound **6a**.

Compound	%	Solvent	GQDs (mg/ml)	Time							comment
				1 min	5 min	30 min	4 h	24 h	48 h	7 days	
6a	1.0	Water	-	I	I	I	I	P	P	P	
6a	1.0	EtOH	-	S	S	S	P	P	P	P	
6a	1.0	MeOH	-	S	S	S	P	P	P	S	
6a	1.0	1-Propanol	-	S	S	S	P	P	P	P	
6a	1.0	Acetone	-	I	I	P	P	P	P	P	
6a	1.0	DMSO	-	S	S	S	S	S	S	S	
6a	1.0	Chloroform	-	I	I	I	I	I	I	I	
6a	1.0	Hexane	-	I	P	P	P	P	P	P	
6a	1.0	Cyclohexane	-	I	P	P	P	P	P	P	
6a	1.0	Cyclohexanone	-	S	S	PG	PG	PG	PG	PG	
6a	1.0	10% EtOH/Water	-	I	P	P	P	P	P	P	
6a	1.0	20% EtOH/Water	-	I	P	P	P	P	P	P	
6a	1.0	50% EtOH/Water	-	S	P	P	P	P	P	P	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



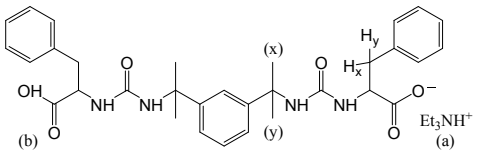
Compound **6a**.

Compound **6a** cannot form a gel in any solvents.

Table S9. Gel formation studies of compound **6b**.

Compound	%	Solvent	GQDs (mg/ml)	Time							comment
				1 min	5 min	30 min	4 h	24 h	48 h	7 days	
6b	1.0	Water	-	S	I	I	I	I	I	I	
6b	1.0	EtOH	-	S	S	S	S	S	S	S	
6b	1.0	MeOH	-	S	S	S	S	S	S	S	
6b	1.0	1-Propanol	-	S	S	S	S	S	S	S	
6b	1.0	Acetone	-	S	S	S	S	S	S	S	
6b	1.0	DMSO	-	S	S	S	S	S	S	S	
6b	1.0	Chloroform	-	S	S	S	P	P	P	P	
6b	1.0	Hexane	-	I	I	P	P	P	P	P	
6b	1.0	Cyclohexane	-	S	I	I	P	P	P	P	
6b	1.0	Cyclohexanone	-	S	S	S	S	S	S	S	
6b	1.0	10% EtOH/Water	-	S	I	I	P	P	P	P	
6b	1.0	20% EtOH/Water	-	S	I	I	P	P	P	P	
6b	1.0	50% EtOH/Water	-	S	S	S	S	S	S	S	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitation from solution



Compound **6b.**

Compound **6b** cannot form a gel in any solvents.

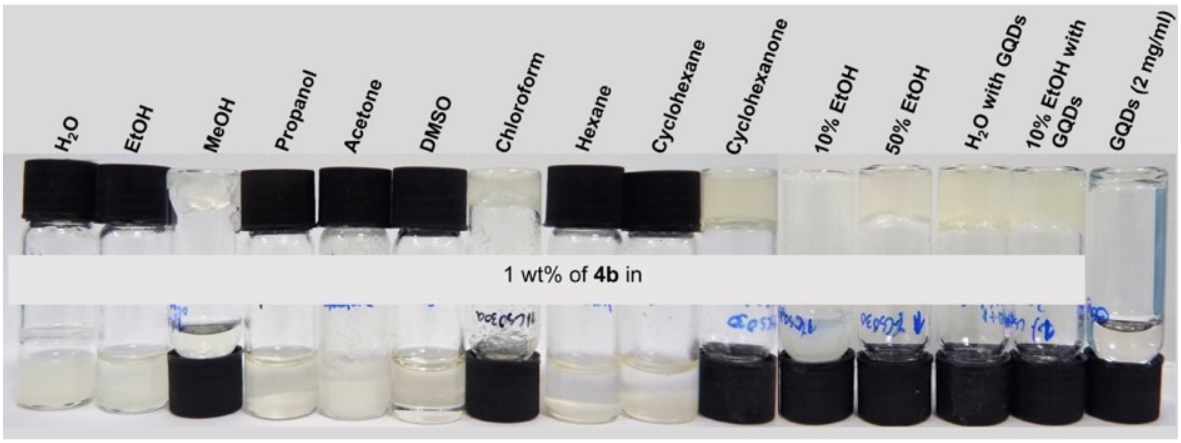


Figure S9. Gel formation from 1wt% solutions of compound **4b** in various solvents.

4. Hybrid GQDs/Gel

4.1 Synthesis of graphene quantum dots

Graphene quantum dots were prepared according to Dong's method [2]. Citric acid (2 g, 0.01 mol) was heated to 200 ^oC for 30 min and the resulting liquid GQDs were added dropwise to 100 mL NaOH solution (10 mg/mL) under vigorous stirring. The pH was adjusted to 8.0 by addition of 1 M HCl solution, and the product was then isolated by dialysis 2,000 Da.

4.2 Preparation of hybrid GQDs/Gel

Preparation of the hybrid GQDs hydrogels (GQDs/Gels) was attempted in two ways as in Supremental data. ; (i) the mixture was sonicated for 30 seconds, followed by heating using heat gun for 30 seconds until it dissolved; (ii) the mixture was sonicated for 30 seconds, followed by heating for 30 seconds until it was dissolved, and followed by a second sonication for 10 seconds.

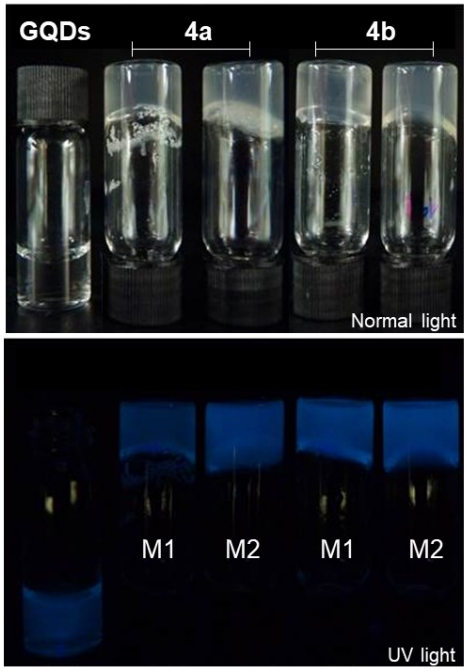


Figure S10. Comparison between hybrid **GQDs/Gels** from **4a** and **4b** that were formed by different procedures: (1) the sample was sonicated for 30 seconds followed by heating for 30 seconds (M1) and (2) the sample was sonicated for 30 seconds followed by heating for 30 seconds and finally sonicating for a further 10 seconds (M2).

Table S10. **GQDs/Gels** formation studies of compound **1-6b**

Compound	**%**	**Solvent**	**GQDs** (mg/ml)	**Time**							**comment**
				1 min	**5 min**	**30 min**	**4 h**	**24 h**	**48 h**	**7 days**	
1	1.0	water	2	I	I	I	I	I	I	I	
2c	1.0	water	2	I	I	I	I	I	I	I	
3	1.0	water	2	I	I	I	I	I	I	I	
4a	1.0	water	2	S	G	**G**	G	G	G	G	
4a	0.5	water	2	S	PG	PG	G	G	G	G	
4a	0.25	water	2	S	PG	PG	PG	PG	PG	PG	
4b	1.0	water	2	G	G	**G**	G	G	G	G	
4b	0. 5	water	2	PG	PG	**G**	G	G	G	G	
4b	0. 25	water	2	S	PG	PG	PG	PG	PG	PG	
4c	1.0	water	2	S	PG	PG	**G**	G	G	G	
4c	0.5	water	2	S	S	S	PG	PG	PG	PG	
4c	0.25	water	2	S	S	S	S	S	PG	PG	
5	1.0	water	2	S	P	P	P	P	P	P	
6a	1.0	water	2	S	P	P	P	P	P	P	
6b	1.0	water	2	S	I	I	I	I	P	P	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitationfrom solution

Table S11. Gel formation studies in a various concentration of gelator **4b** and GQDs.

%	Gelator	Solvent	GQDs (mg/ml)	Time							comment
				1 min	5 min	30 min	4 h	24 h	48 h	7 days	
0.3	**4b**	10 mM Phosphate pH8	-	S	PG	PG	PG	PG	PG	PG	
0.5	**4b**	10 mM Phosphate pH8	-	S	PG	PG	PG	PG	PG	PG	
1	**4b**	10 mM Phosphate pH8	-	S	PG	PG	PG	PG	PG	PG	
2	**4b**	10 mM Phosphate pH8	-	S	PG	**G**	G	G	G	G	Opaque
3	**4b**	10 mM Phosphate pH8	-	S	G	**G**	G	G	G	G	Opaque
0.3	**4b**	10 mM Phosphate pH8	2	S	PG	PG	G	G	G	G	
0.5	**4b**	10 mM Phosphate pH8	2	S	PG	**G**	G	G	G	G	
1	**4b**	10 mM Phosphate pH8	2	S	G	**G**	G	G	G	G	Robust
2	**4b**	10 mM Phosphate pH8	2	S	G	**G**	G	G	G	G	Opaque
3	**4b**	10 mM Phosphate pH8	2	S	G	**G**	G	G	G	G	Opaque
0.3	**4b**	10 mM Phosphate pH8	0	S	PG	PG	PG	PG	PG	PG	
0.3	**4b**	10 mM Phosphate pH8	0.5	S	PG	PG	PG	PG	PG	G	
0.3	**4b**	10 mM Phosphate pH8	1	S	PG	PG	PG	G	G	G	
0.3	**4b**	10 mM Phosphate pH8	2	S	PG	PG	G	G	G	G	
0.3	**4b**	10 mM Phosphate pH8	3	S	PG	PG	G	G	G	G	
0.5	**4b**	10 mM Phosphate pH8	0	S	PG	PG	PG	PG	PG	PG	
0.5	**4b**	10 mM Phosphate pH8	0.5	S	PG	PG	PG	PG	G	G	
0.5	**4b**	10 mM Phosphate pH8	1	S	PG	PG	G	G	G	G	
0.5	**4b**	10 mM Phosphate pH8	2	S	PG	**G**	G	G	G	G	
0.5	**4b**	10 mM Phosphate pH8	3	S	PG	**G**	G	G	G	G	
1	**4b**	10 mM Phosphate pH8	0	S	PG	PG	PG	PG	PG	PG	
1	**4b**	10 mM Phosphate pH8	0.5	S	PG	PG	PG	PG	G	G	
1	**4b**	10 mM Phosphate pH8	1	S	PG	**G**	G	G	G	G	Robust
1	**4b**	10 mM Phosphate pH8	2	S	G	**G**	G	G	G	G	Robust
1	**4b**	10 mM Phosphate pH8	3	S	G	**G**	G	G	G	G	Robust

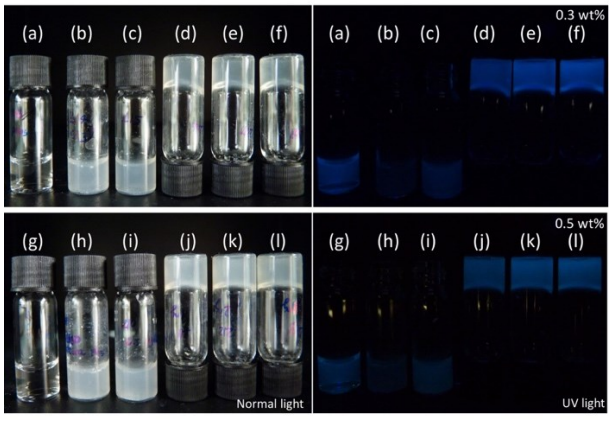


Figure S11. 2 mg/ml of GQDs solution (a, g); and 0 (b), 0.5 (c), 1 (d), 2 (e) and 3 mg/ml (f) of GQDs in 0.3wt% of **4b**; and 0 (h), 0.5 (i), 1 (j), 2 (k) and 3 mg/ml (l) of GQDs in 0.5 wt% of **4b** in 10 mM phosphate pH 8 for 24 h. The left picture was taken in visible light and the right picture was taken in UV light.

Table S12. Gel formation studies of gelators **4a-4c** in a range of pH between 6-9.

Gelator	**%**	**Solvent**	**GQDs (mg/ml)**	**Time**					**comment**
				1 min	**5 min**	**30 min**	**24 h**	**7 days**	
4a	0.5	Water	-	I	I	I	I	I	
4a	0.5	Water	2	S	PG	PG	G	G	
4a	0.5	10 mM Phosphate pH6	2	S	PG	PG	G	G	
4a	0.5	10 mM Phosphate pH7	2	S	PG	PG	G	G	
4a	0.5	10 mM Phosphate pH8	2	S	PG	PG	G	G	
4a	0.5	10 mM Tris pH8	2	S	PG	PG	PG	G	**4a** is not all dissolved
4a	0.5	10 mM Tris pH9	2	S	PG	PG	PG	G	
4b	0.5	Water	-	PG	PG	PG	PG	PG	
4b	0.5	Water	2	PG	PG	**G**	G	G	
4b	0.5	10 mM Phosphate pH6	2	S	PG	PG	G	G	
4b	0.5	10 mM Phosphate pH7	2	S	PG	PG	G	G	
4b	0.5	10 mM Phosphate pH8	2	S	PG	**G**	G	G	
4b	0.5	10 mM Tris pH8	2	S	PG	**G**	G	G	**4b** is not all dissolved
4b	0.5	10 mM Tris pH9	2	S	PG	PG	PG	G	
4c	0.5	Water	-	S	S	S	S	PG	
4c	0.5	Water	2	S	S	PG	PG	PG	
4c	0.5	10 mM Phosphate pH8	2	S	S	PG	G	G	

G = gel, PG = partial gel, CG = collapsed gel, S = Solution, I = insoluble, P = rapid precipitationfrom solution

Table S13. Gel formation studies of gelators **4a-4c** in different concentration of phosphate buffer pH 8

Gelator	%	Concentration of phosphate buffer pH8 (mM)	GQDs (mg/ml)	pH (Measured)	Time			comment
					1 min	5 min	30 min	
4a	0.5	-	-	4.87	I	I	I	
4b	0.5	-	-	7.52	S	PG	PG	
4c	0.5	-	-	9.98	S	S	S	
4a	0.5	10	-	7.71	S	PG	PG	
4b	0.5	10	-	7.80	S	PG	PG	
4c	0.5	10	-	8.78	S	S	S	
4a	0.5	25	-	7.89	S	PG	G	
4b	0.5	25	-	7.97	S	G	G	Robust
4c	0.5	25	-	8.62	S	S	PG	
4a	0.5	50	-	7.86	S	G	G	
4b	0.5	50	-	7.93	S	G	G	Opaque
4c	0.5	50	-	8.41	S	PG	PG	Opaque
-	0.0	-	4	7.70	-	-	-	
4a	0.5	10	2	7.76	S	PG	PG	
4b	0.5	10	2	7.84	S	PG	**G**	Robust
4c	0.5	10	2	8.68	S	S	PG	
4a	0.5	25	2	7.83	S	G	G	Robust
4b	0.5	25	2	7.90	S	G	G	Robust
4c	0.5	25	2	8.42	S	PG	PG	
4a	0.3125	12.5	1.25	7.84	S	PG	PG	
4b	0.3125	12.5	1.25	7.93	S	PG	**G**	
4c	0.3125	12.5	1.25	8.17	S	S	S	

5. Rheology of GQDs/Gels

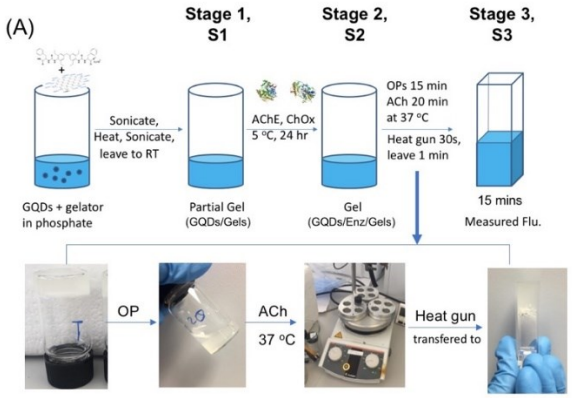
Rheological measurements were carried out using an AR2000 rheometer equipped with a rough Peltier plate, 25 mm rough plate geometry, and 2.5 mm gap. Samples were prepared by boiling gelator solutions in sealed glass vials. The hot solutions were then poured into a 25 mm cylindrical glass mould on the Peltier plate and the gels allowed to form over 30 minutes prior to analysis, after which time the mould was removed. The materials were cooled to 10 ^{o}C throughout formation and analysis in order to minimise evaporation of the gel solvent. Frequency sweep experiments were performed at a constant oscillation stress of 0.5 Pa and a

variable angular frequency of 0.1–100 rad/sec. The stress sweep was performed at a constant angular frequency of 1 Pa variable oscillation stress of 0.1–1000 Pa.

6. Hybrid GQDs/Enz/Gel materials

6.1 Preparation of hybrid GQDs/Enz/Gel materials

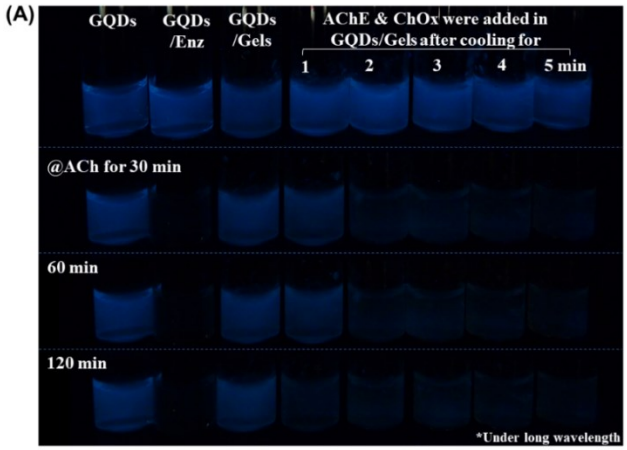
The enzyme-loaded PL sensing hybrid gel materials (GQD/Enz/Gel) were prepared in three stages (S1 – S3). in three stages (S1 – S3). In stage 1 (S1), the partial gels of the integrated gelator and GQDs were prepared as shown in Figure S14A. After 5 min, AChE and ChOx in phosphate buffer were added to the partial gels at a variety of temperatures (see Figure S15) and materials were then left for 24 h at 5 °C until complete gel formation had occurred, defined as stage 2 (S2). In the final stage (S3), the GQDs/Enz/Gels were incubated with analyte (*vide infra*).



(B)

	Stage 1 (GQDs/Gels)	Stage 2 (GQDs/Enz/Gels)	Stage 3 OPs detection
GQDs (mg/ml)	2.00	1.67	1.25
Gelator (wt%)	0.50	0.4167	0.3125
Phosphate buffer pH 8 (mM)	10.00	16.67	12.50
AChE (U/ml)	-	1.67	1.25
ChOx (U/ml)	-	0.4167	0.3125
OPs (M)	-	-	$1.25x10^{-9} - 1.25x10^{-4}$
ACh (mM)	-	-	5.00
V. final (ml)	1.0	1.2	1.6

Figure S14. Preparation (A) and final concentration (B) of **GQDs/Enz/Gels** before and after detection.



(B)

Time after cooling (min)	Temperature of gels (°C)
0	70.0
1	50.0
2	32.5
3	25.3
4	22.3
5	21.3
6	20.7
10	20.3
15	19.9

Figure S15. (A) The fluorescent images of **GQDs/Enz/Gels** after incubation in acetylcholine for 30, 60 and 120 mins, they were prepared by cooling the GQDs/Gels for 1 to 5 min before

adding the enzymes. (B) The table shows the temperature of GQDs/Gel after cooling at room temperature for 0-15 min.

In stage 2 (**GQDs/Enz/Gels**), 0.1 mL of AChE and ChOx added to 0.5 mL of partial **GQDs/Gels** as a function of time. The partial gels were cooled to ambient temperature, and then the resulting **GQDs/Enz/Gels** were stored at 5 ^{o}C for 24 h. 0.1 mL of 10 mg/mL (55 mM) acetylcholine (ACh) was added to the sample. and The enzyme activity was monitored using the naked-eye, through exposure to a UV-lamp (λ_{ex} 365 nm) for 30, 60 and 120 min. The results are shown in Figure S6. After reaction with ACh for 30 min, images of the **GQDs/Enz/Gels** showed significantly less PL than **GQDs/Gels** samples which had been cooled for 2-5 min, without the addition of Ach. These results suggest a temperature-dependent enzymatic activity which can function at temperatures lower than 37 ^{o}C. The enzyme-free system was cooled for 2-5 min which means its temperature would be between of 32.5 – 21.3 ^{o}C, a suitable range for enzyme activity. However, to be certain that the system was not too hot before adding the enzyme, a cooling time of 5 min was selected for further experiments.

6.2 Inhibition efficiency

Inhibition efficiency was calculated *via* equation (S1), where $K_{20without}$ and $K_{20withOP}$ are the photoluminescent quenching with and without OPs after incubation in ACh for 20 min (K_{20} = F_0-F_{20}/20, where F_0 and F are the PL intensity of **GQDs/Enz/Gels** in the presence and absence of ACh followed by incubation for 20 min) [3].

$$I(\%) = \left(\frac{K_{20without} - K_{20withOP}}{K_{20without}}\right) \times 100 \qquad (S1)$$

7. Scanning electron microscopy

The **GQDs/Gels** and **GQDs/Enz/Gels** samples were prepared and cooled at room temperature for 1 and 30 min, respectively, then dropped onto a glass slide and dried in air, at room temperature for 2 days. The samples were coated with Au ions and imaged using a JSM-IT100 scanning electron microscope. The average diameter of the gel fibers was obtained by measuring 100 fibers per SEM image using ImageJ software (ImageJ 1.49 V free software with Java 1.6.0 65(32-bit) obtained from https://imagej. nih.gov/ij/, Wayne Rasband, National Institutes of Health, USA).

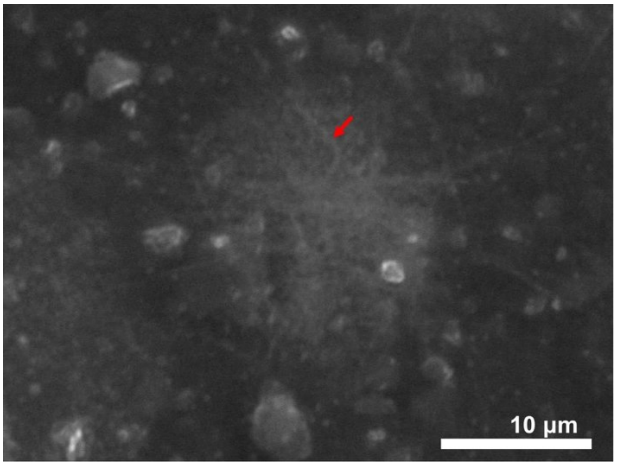


Figure S16. SEM image of a dried xerogel containing gelator **4b** (0.5 wt%) in 10 mM phosphate buffer.

8. ATR-FTIR spectra

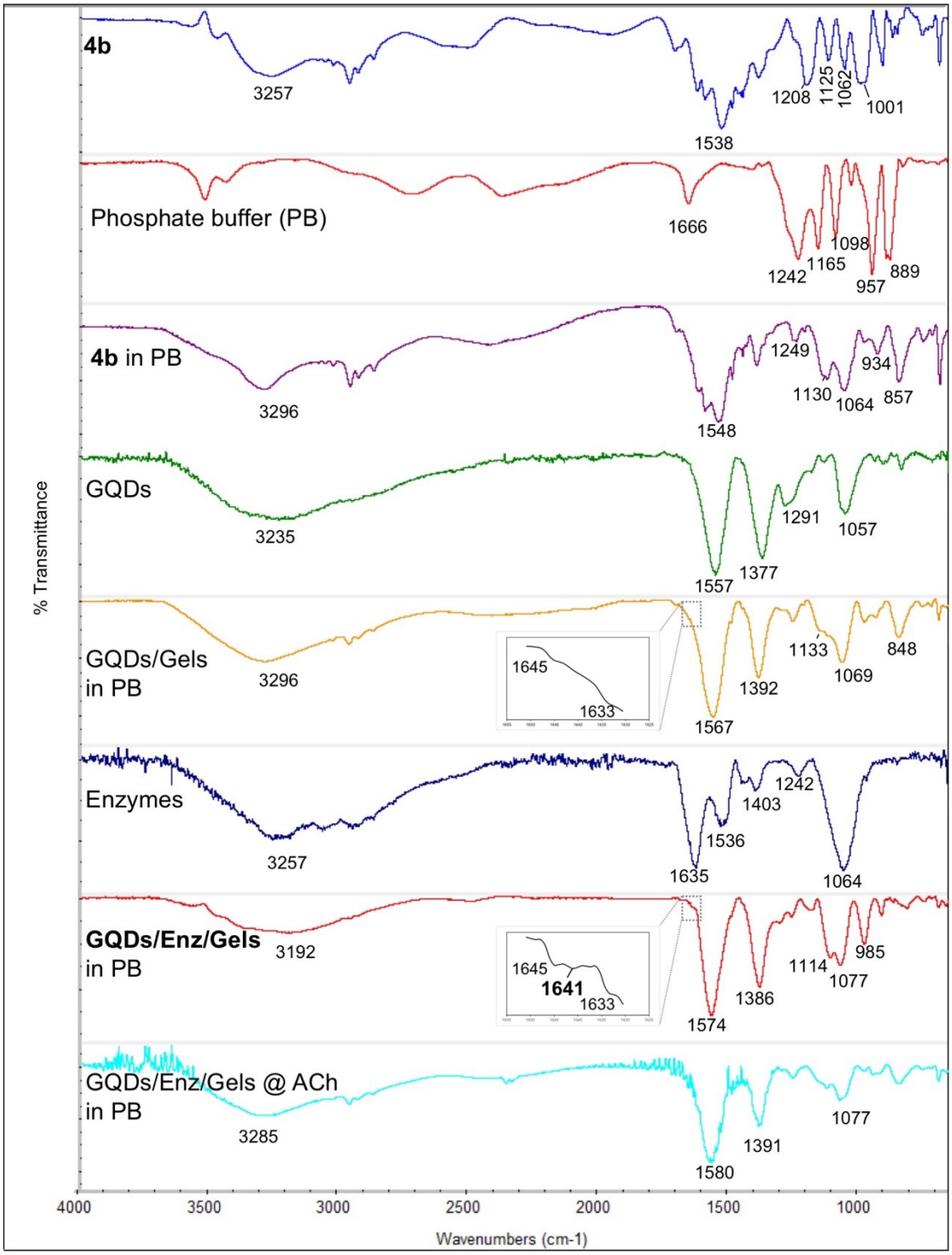


Figure S17. ATR-FTIR spectra of the individual components and xerogel of the hybrid hydrogels. Xerogels were formed by freeze drying for one week.

The spectra of these hybrid materials show a board absorption band at 3000-3500 cm^{-1} (NH and OH stretch), and peaks at 1633-1645 cm^{-1} (ν_{CO} and ν_{CN} of amide I of enzymes), 1574 cm^{-1} (ν_{asCOO}- of GQDs), 1574-1496 (δ_{NH} and ν_{CN} of urea in gelator **4b** and amide II of enzymes)[4, 5] as well as 1386 cm^{-1} (ν_{sCOO}-) and 1077 cm^{-1} ($\nu_{C\text{-}OH}$)[2], belonging to the characteristic peak of -COOH and -OH group of the edge of GQDs, respectively. Additionally, the appearance of a small peak at 1641 cm^{-1} and the peak at 1574 cm^{-1} are indicative of an amide I and amide II, respectively, of the enzyme backbone [4, 5]. The low intensity of peaks assigned to the enzymes is likely to be caused by their very low concentration compared to the GQDs and gelator **4b** in these materials.

9. H_2O_2-responsive studies

The H_2O_2-responsive behavior of the hybrid **GQDs/Gels** was studied by following their photoluminescence intensity at 465 nm. Initially, 0.2 mL of H_2O_2 at various concentrations, and 0.2 mL of water were added to 1.2 mL of **GQDs/Gels** in a sealed vial and incubated at 37 ^oC for 20 min. The sample was then heated to dissolve, transferred to a cuvette and left for 15 min under ambient conditions, before the measurement of photoluminescence intensity. The **GQDs/Gels** were studied using the final concentrations of 1.25 mg/ml of GQDs and 0.3125 %wt of **4b** in 12.5 mM phosphate buffer.

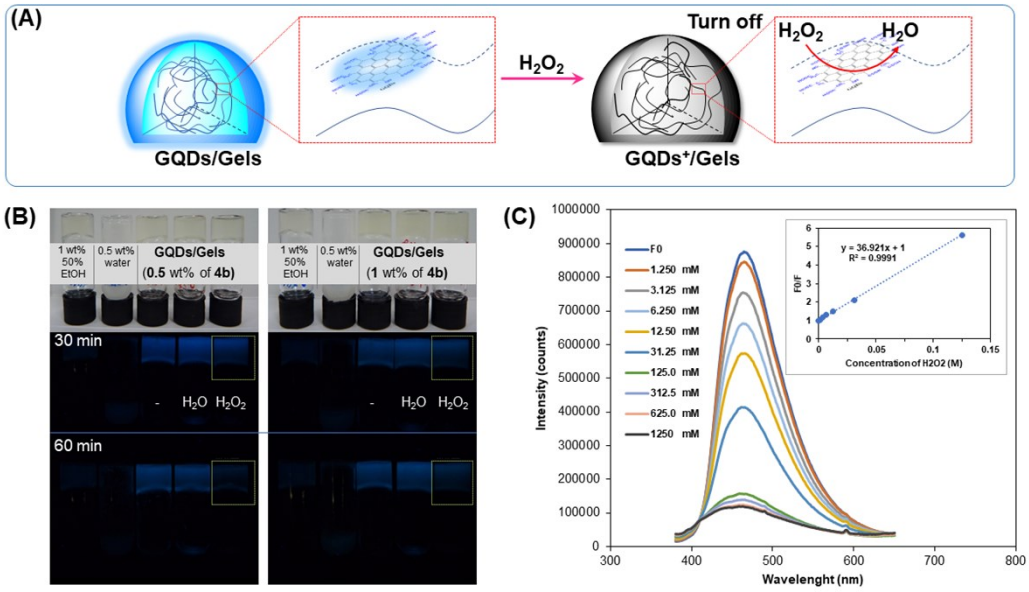


Figure S18. (**A**) Illustration of peroxidase-catalytic reaction of **GQDs/Gels. (B)** Comparison between concentration of **4b** (0.5 and 1 wt%) toward naked eye brightness quenching by slow passage of H_2O_2 from top to bottom of vial at room temperature. (**C**) Concentration-dependent PL changes of **GQDs/Gels** after interaction with H_2O_2 between 0 and 1250 mM at 37 ^oC for

20 min. Inset of C is Stern-Volmer plots from PL of **GQDs/Gels** after interaction with H_2O_2 at concentration ranging from 0 to 125 mM.

$$acetylcholine + H_2O \xrightarrow{AChE} choline + acetate \quad (S3)$$

$$choline + O_2 \xrightarrow{ChOx} H_2O_2 \quad (S4)$$

9.Fluorescence responses of materials

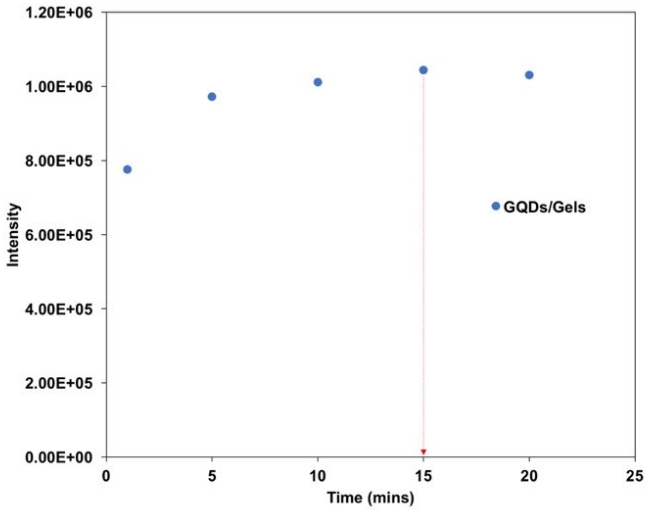


Figure S19. Fluorescence intensity of **GQDs/Gels** from gelator **4b** proved to be constant after re-heating and allowing the gel to reform in a cuvette for 15 minutes. The **GQDs/Gels** sample was prepared under condition of 1.25 mg/ml of GQDs with 0.3125 wt% of **4b** in 12.5 mM phosphate buffer pH 8.

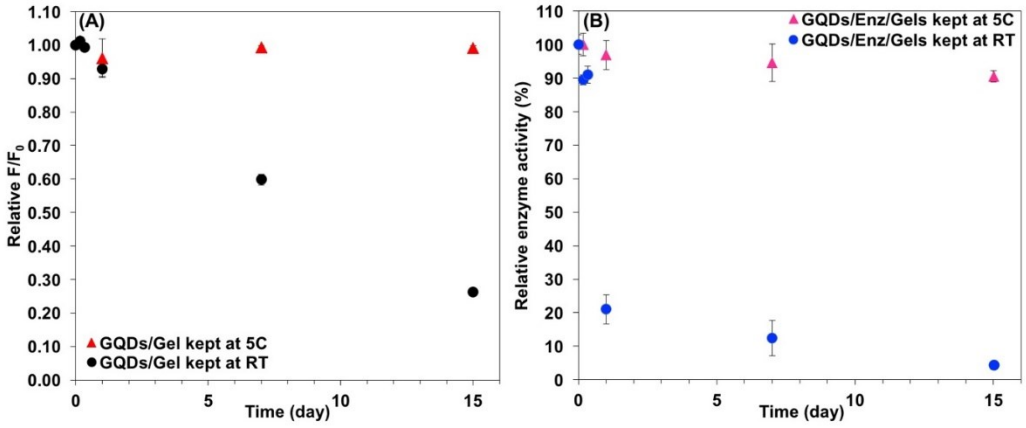


Figure S20. (A) Relative F/F_0 of **GQDs/Gels**. (B) Relative enzyme activity (%) of **GQDs/Enz/Gels** that were kept at 5 ^oC and room temperature, from 4h to 15 days.

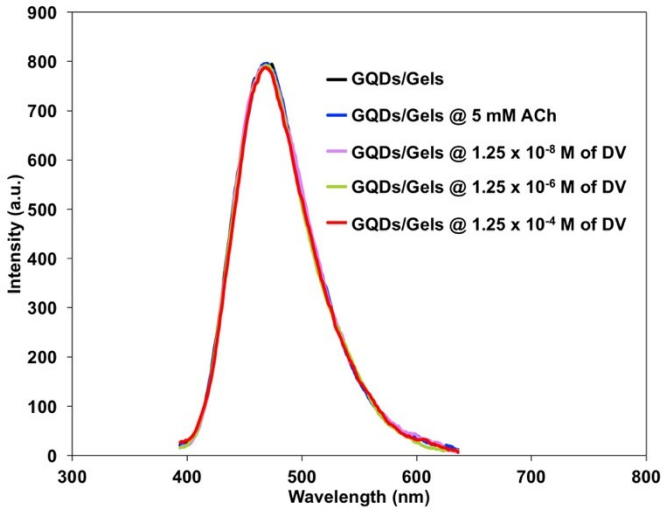


Figure S21. Fluorescence intensity of **GQDs/Gels** without enzyme after addition of ACh and dichlorvos (DV) in a range of 1.25 x 10^{-8} to 1.25 x 10^{-4} M.

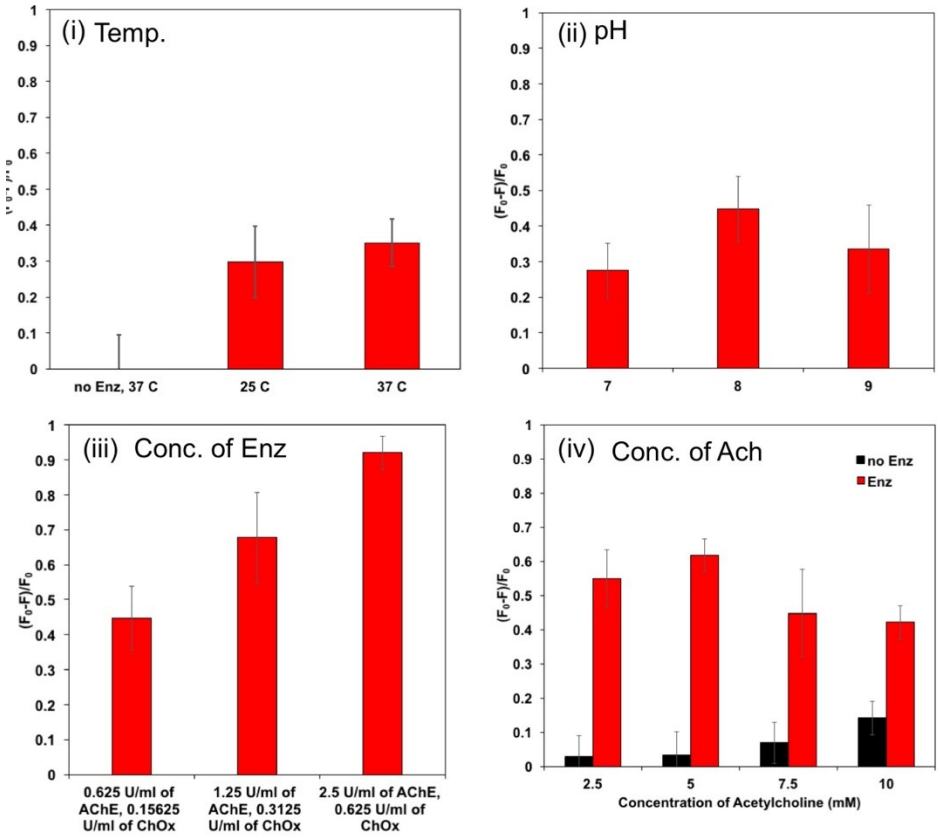


Figure S22. Optimized condition temperature (i), pH (ii) and the concentration of both enzymes and acetylcholine, for the final sensor system with a 5 mM concentration of ACh (iii) and the comparison of **GQDs/Gels** and **GQDs/Enz/Gels** in various concentration of Ach (iv). The normalized PL intensity (F_0-F/F_0), where F_0 and F are PL intensity of **GQDs/Gels** and **GQDs/Enz/Gels**, respectively.

10. The green value from naked-eye image

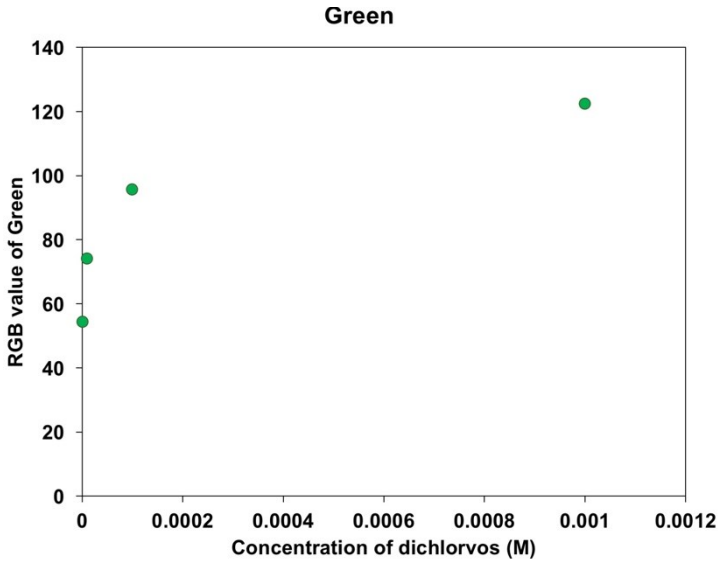


Figure S23. Green component of the RGB value for 50 μL **GQDs/Enz/Gels** on a glass slide, 2h after the addition of 10 μL of dichlorvos (DV) in a range of $1x10^{-6}$ to $1x10^{-3}$ M, followed by 10 μL of 80 mM ACh. The final concentration of these hydrogels is 1.25 mg/mL of GQDs, 0.3125%wt of **4b**, 20 U/mL of AChE and 2 U/mL of ChOx.

11. References

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