

Supporting Information

Charge-tunable graphene dispersions in water made with amphoteric pyrene derivatives

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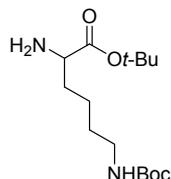
S1. Synthesis and Characterisation of Pyrene Derivatives

S1.1 General Information

Tetrahydrofuran (THF) and toluene were dried using a PureSolv solvent purification system. All other solvents and reagents used were purchased from commercial suppliers and used without further purification. ¹H-NMR spectra were obtained at room temperature on a Bruker 400 MHz or 500 MHz spectrometer. ¹³C-NMR spectra were obtained at 100 or 125 MHz respectively. All NMR spectra were processed using *MestReNova* NMR software. Chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) reported in Hz. Splitting patterns are reported as follows: singlet (s), doublet (d), triplet (t), quadruplet (q), quintuplet (quint), doublet of doublets (dd), doublet of doublets of doublets (ddd), multiplet (m), etc. NMR signals were assigned using the appropriate 2D NMR experiments (*i.e.* HSQC and HMBC when necessary). TLC analysis was carried out on aluminium sheets coated with silica gel and visualised using potassium permanganate solution and/or UV light. Infra-red spectra were recorded as evaporated films or neat using FTIR spectroscopy. Melting points were measured on solids as obtained after the purification method reported below. Mass spectra were obtained using positive or negative electrospray (ESI), atmospheric pressure chemical ionization (APCI) or atmospheric solids analysis probe (ASAP).

S1.2. Synthesis and Characterisation

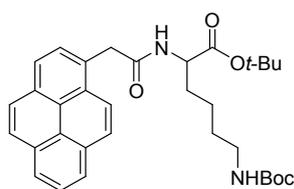
tert-Butyl *N*⁶-(*tert*-butoxycarbonyl)lysinate (S1)



To a flask charged with a solution of *tert*-butyl *N*²-(((9H-fluoren-9-yl)methoxy)carbonyl)-*N*⁶-(*tert*-butoxycarbonyl)lysinate¹ (820 mg, 1.56 mmol) in dry CH₂Cl₂ (6.3 mL) under nitrogen was added piperidine (3.9 mL, 39.1 mmol). After 2 h stirring at room temperature the reaction mixture was diluted with toluene and volatiles were removed under vacuum. The crude product was purified by silica column chromatography (CH₂Cl₂/MeOH, 100:0 to 90:10) to yield the title product as a yellow oil (343 mg, 73%). ¹H-NMR (400 MHz, CDCl₃) δ 1.33-1.63 (m, CHCO₂C(CH₃)₃ + NHCO₂C(CH₃)₃ + 2 × CH₂ + CHCH_aH_b, 23 H), 1.65-1.79 (m, CHCH_aH_b, 1 H), 3.04-3.20 (m, CH₂, 2 H), 3.25-3.44 (m, CHCO₂*t*-Bu, 1 H), 4.55 (bs, NHBoc, 1 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 22.9 (CH₂), 28.1 (C(CH₃)₃), 28.4 (C(CH₃)₃), 29.8 (CH₂), 34.6 (CH₂), 40.4 (CH₂NHBoc), 54.5 and 54.9 (CHCO₂*t*-Bu), 79.1 (C(CH₃)₃), 80.9 (C(CH₃)₃), 155.9 (NHCO₂*t*-Bu), 175.4 and 175.6 (CHCO₂*t*-Bu) ppm; IR ν_{max} (neat/cm⁻¹): 3369, 2976, 2933, 2863, 1711, 1522, 1366, 1249, 1157; HRMS calcd for C₁₅H₃₁O₄N₂ [M+H]⁺: 303.2278, found 303.2275.

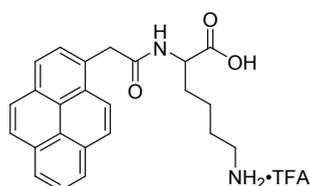
¹ *N*²-(((9H-fluoren-9-yl)methoxy)carbonyl)-*N*⁶-(*tert*-butoxycarbonyl)lysinate was prepared according to a reported procedure: A. Pratesi, M. Ginanneschi, F. Melani, M. Chinol, A. Carollo, G. Paganelli, M. Lumini, M. Bartoli, M. Frediani, L. Rosi, G. Petrucci, L. Messori, A. M. Papini, *Org. Biomol. Chem.* **2015**, *13*, 3988.

tert-Butyl *N*⁶-(tert-butoxycarbonyl)-*N*²-(2-(pyren-1-yl)acetyl)lysinate (S2**) (amide formation)**



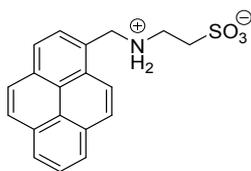
To a flask charged with 1-pyrenylacetic acid (78 mg, 0.301 mmol), and HOBt (51 mg, 0.331 mmol) under nitrogen was added a solution of **S1** (100 mg, 0.331 mmol) in dry THF (0.6 mL). The resulting mixture was stirred at room temperature for 30 min before adding *N,N'*-diisopropylcarbodiimide (51 μ L, 0.331 mmol). The mixture was stirred at room temperature for 22 h before diluting it with Et₂O and filtering it through cotton with more Et₂O. The solution was washed with aqueous 2 M HCl, saturated aqueous NaHCO₃ and brine, dried (MgSO₄) and concentrated under vacuum. The crude product was purified by silica column chromatography (hexane/EtOAc, 80:20 to 50:50) to obtain the title compound as a tan solid (146 mg, 89%), mp (CH₂Cl₂): 126-128 °C. ¹H-NMR (400 MHz, CDCl₃) δ 0.90-1.11 (m, CH₂ + CH_aH_b, 3 H), 1.15-1.53 (m, CHCO₂C(CH₃)₃ + NHCO₂C(CH₃)₃ + CH_aH_b + CH_aH_b, 20 H), 1.61-1.74 (m, CH_aH_b, 1 H), 2.65-2.97 (m, CH₂NHBoc, 2 H), 4.22-4.43 (m, ArCH₂ + NHBoc, 3 H), 4.43-4.52 (m, CHCO₂*t*-Bu, 1 H), 5.81 (d, *J* = 8.0 Hz, NHCHCO₂*t*-Bu, 1 H), 7.97 (d, *J* = 7.6 Hz, ArH, 1 H), 8.02-8.13 (m, ArH, 3 H), 8.15-8.26 (m, ArH, 5 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 22.0 (CH₂), 27.8 (C(CH₃)₃), 28.4 (C(CH₃)₃), 29.3 (CH₂), 32.1 (CH₂), 40.1 (CH₂NHBoc), 42.1 (ArCH₂CONH), 52.4 (CHCO₂*t*-Bu), 79.0 (C(CH₃)₃), 82.0 (C(CH₃)₃), 123.0 (ArCH), 124.6 (ArC), 125.1 (ArC), 125.2 (ArCH), 125.3 (ArCH), 125.4 (ArCH), 126.2 (ArCH), 127.4 (ArCH), 127.5 (ArCH), 128.3 (ArCH), 128.3 (ArC), 128.5 (ArCH), 129.5 (ArC), 130.8 (ArC), 131.1 (ArC), 131.3 (ArC), 155.8 (NHCO₂*t*-Bu), 170.5 (CHCO₂*t*-Bu), 170.9 (CH₂CONH) ppm; IR ν_{\max} (neat/cm⁻¹): 3323, 2974, 2934, 1713, 1652, 1512, 1366, 1248, 1162; HRMS calcd for C₃₃H₄₀O₅N₂Na [M+Na]⁺: 567.2829, found 567.2829.

5-Carboxy-5-(2-(pyren-1-yl)acetamido)pentan-1-aminium trifluoroacetate (py-lys) (acid and amine deprotection)



To a vial charged with a solution of **S2** (33 mg, 0.060 mmol), in CH₂Cl₂ (0.75 mL) was added trifluoroacetic acid (190 μ L), the vial was sealed under air and the mixture was stirred at room temperature. After 17 h volatiles were removed under vacuum, the residue was dissolved in as little THF as possible and this was added onto Et₂O (10 mL). The cloudy suspension was allowed to settle before removing the supernatant. After drying under vacuum the title product was obtained as a pale brown solid (28 mg, 93%), mp (Et₂O): 116-119 °C. ¹H-NMR (500 MHz, MeOD-*d*₄) δ 1.30-1.48 (m, CH₂, 2 H), 1.49-1.67 (m, CH₂, 2 H), 1.68-1.82 (m, CH_aH_b, 1 H), 1.84-2.01 (m, CH_aH_b, 1 H), 2.66-2.84 (m, CH₂NH₃, 2 H), 4.31-4.38 (m, ArCH₂CONH, 2 H), 4.39-4.50 (m, NHCHCO₂H, 1 H), 7.99-8.12 (m, ArH, 4 H), 8.14-8.25 (m, ArH, 4 H), 8.36 (d, *J* = 9.2 Hz, ArH, 1 H) ppm; ¹³C-NMR (125 MHz, MeOD-*d*₄) δ 23.7 (CH₂), 27.8 (CH₂), 32.2 (CH₂), 40.4 (CH₂NH₃), 41.4 (ArCH₂CONH), 53.1 (NHCHCO₂H), 124.6 (ArCH), 125.8 (ArC), 126.0 (ArCH), 126.1 (ArCH), 126.1 (ArC), 126.3 (ArCH), 127.2 (ArCH), 128.3 (ArCH), 128.5 (ArCH), 128.7 (ArCH), 129.7 (ArCH), 130.8 (ArC), 130.8 (ArC), 132.1 (ArC), 132.2 (ArC), 132.8 (ArC), 174.1 (CO), 175.1 (CO) ppm; IR ν_{\max} (neat/cm⁻¹): 3044, 2942, 1674, 1652, 1538, 1436, 1436, 1202, 1184, 1135; HRMS calcd for C₂₄H₂₄O₃N₂Na [M+Na]⁺: 411.1679, found 411.1677.

2-((Pyren-1-ylmethyl)ammonio)ethane-1-sulfonate (py-tau)

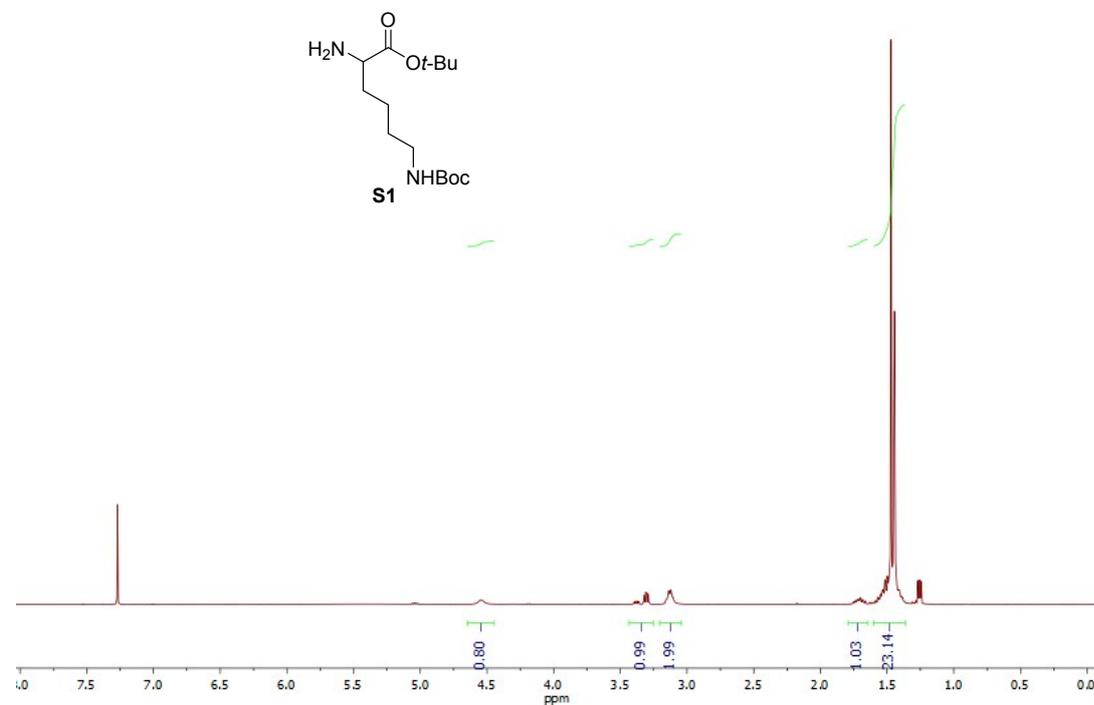


To a stirring suspension of taurine (543 mg, 4.34 mmol) and sodium hydroxide (174 mg, 4.34 mmol) in dry EtOH (26 mL) was added pyrene-1-carboxaldehyde (1.00 g, 4.34 mmol). The mixture was refluxed under N₂ for 2 h before cooling to room temperature. Then, sodium borohydride (174 mg, 4.60 mmol) was added in one portion and the mixture was refluxed again. After 22 h the mixture was allowed to cool to room temperature and was acidified with acetic acid (15 mL). The volume of the resulting suspension was reduced by half under reduced pressure before adding Et₂O. The solid thus obtained filtered under vacuum and washed with more Et₂O. The bright yellow solid thus obtained was then re-suspended in CH₂Cl₂ (25 mL) and refluxed for 15 min. After cooling to room temperature the solid was filtered under vacuum and washed with CH₂Cl₂, H₂O and acetone. The title product was obtained as a yellow solid (698 mg, 47%), mp (CH₂Cl₂) >260 °C. ¹H-NMR (400 MHz, CDCl₃) δ 2.91 (t, *J* = 6.8 Hz, CH₂CH₂SO₃⁻, 2 H), 3.36-3.49 (m, CH₂CH₂SO₃⁻, 2 H), 5.02 (t, *J* = 5.2 Hz, ArCH₂NH₂⁺, 2 H), 8.14 (t, *J* = 7.6 Hz, ArH, 1 H), 8.20-8.31 (m, ArH, 3 H), 8.33-8.43 (m, ArH, 4 H), 8.59 (d, *J* = 9.2 Hz, ArH, 1 H), 8.83-9.01 (m, ArCH₂NH₂⁺, 2 H) ppm; ¹³C-NMR (125 MHz, CDCl₃) δ 44.1 (CH₂CH₂SO₃⁻), 46.6 (CH₂CH₂SO₃⁻), 47.1 (ArCH₂NH₂⁺), 123.2 (ArCH), 123.6 (ArC), 123.9 (ArC), 124.9 (ArCH), 125.5 (ArC), 125.7 (ArCH), 125.9 (ArCH), 126.6 (ArCH), 127.3 (ArCH), 128.2 (ArCH), 128.3 (ArCH), 129.1 (ArCH), 129.4 (ArC), 130.2 (ArC), 130.7 (ArC), 131.5 (ArC) ppm; IR ν_{max} (neat/cm⁻¹): 3178, 3043, 2820, 1687, 1595, 1440, 1256, 1207, 1177, 1050, 842; HRMS calcd for C₁₉H₁₆O₃NS [M-H]⁻: 338.0856, found 338.0866.

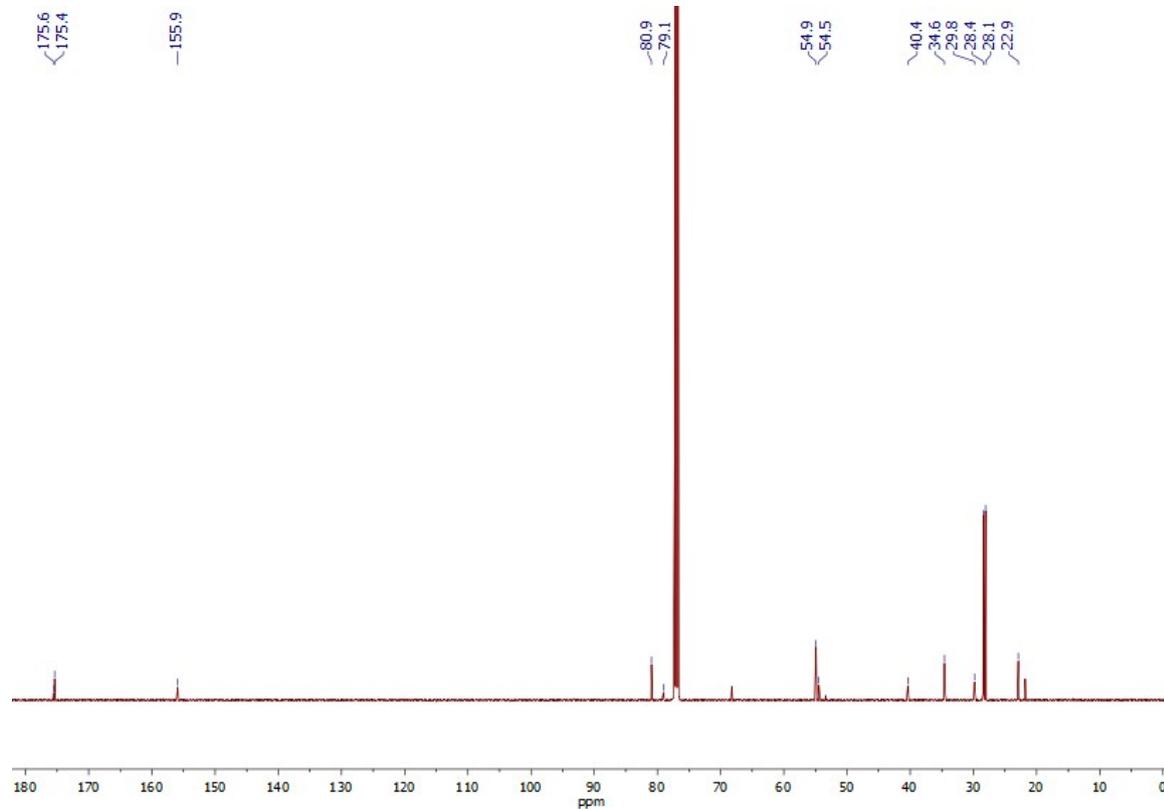
S1.3. NMR Spectra

tert-Butyl *N*⁶-(*tert*-butoxycarbonyl)lysinate (S1)

¹H-NMR (400 MHz, CDCl₃)

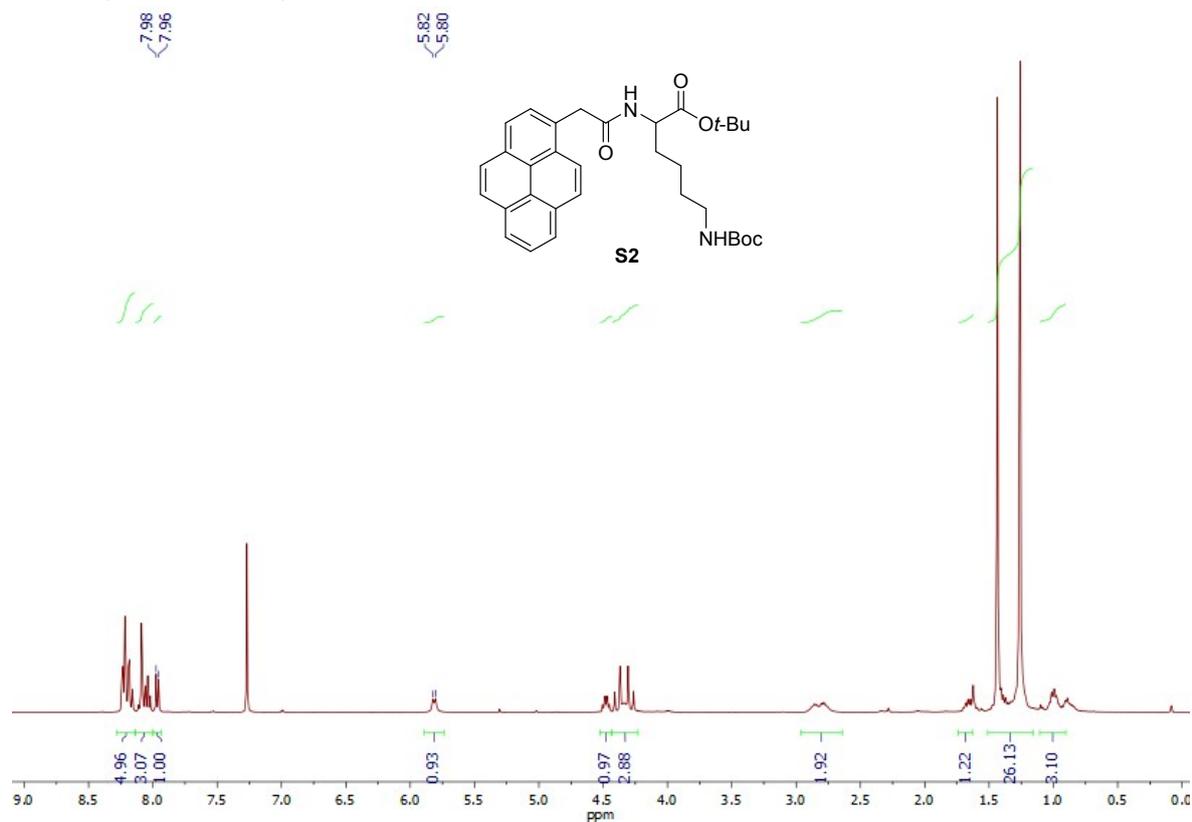


¹³C-NMR (125 MHz, CDCl₃)

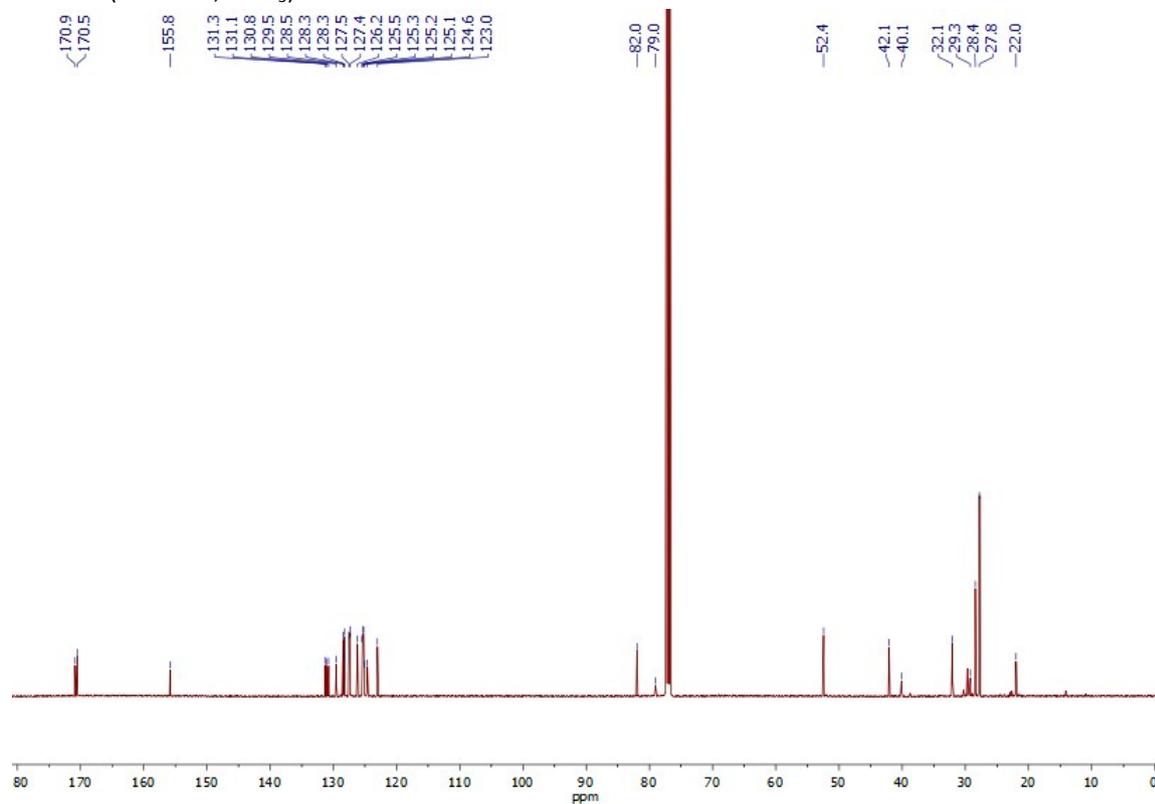


***tert*-Butyl *N*⁶-(*tert*-butoxycarbonyl)-*N*²-(2-(pyren-1-yl)acetyl)lysinate (S2)**

¹H-NMR (400 MHz, CDCl₃)

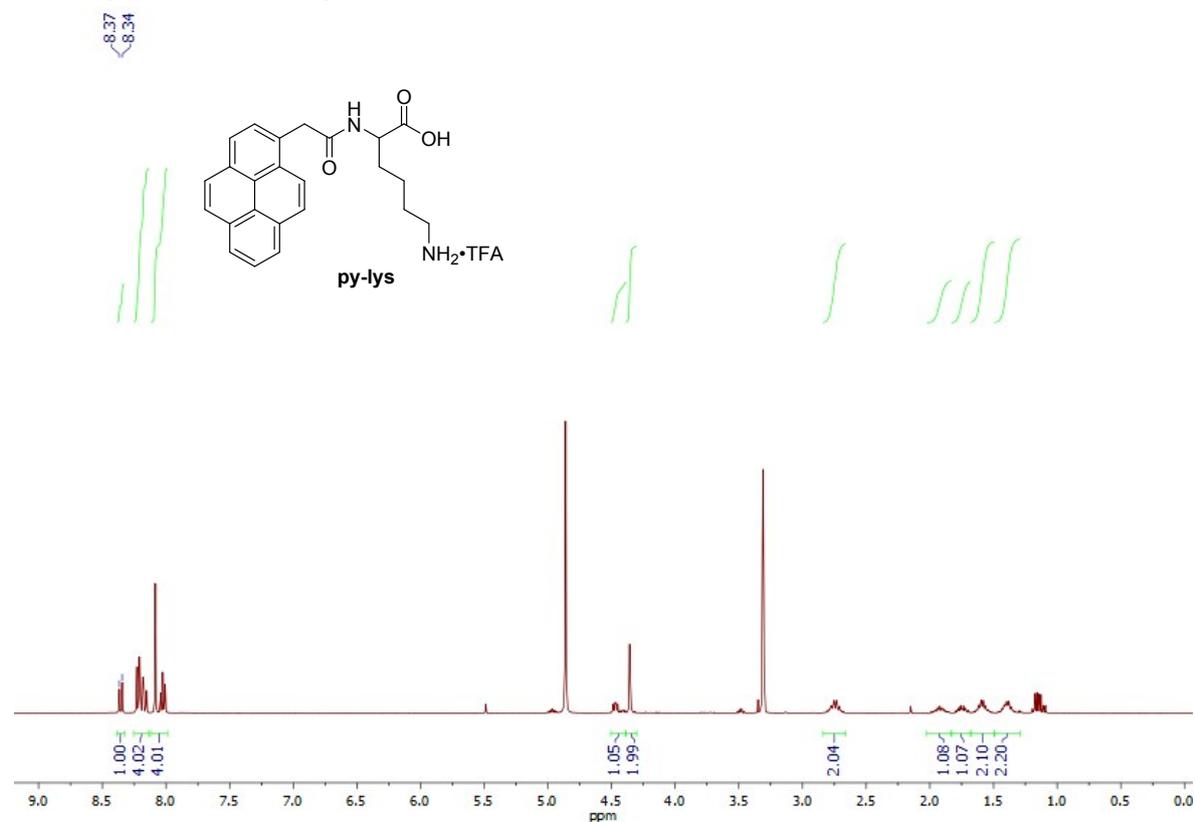


¹³C-NMR (125 MHz, CDCl₃)

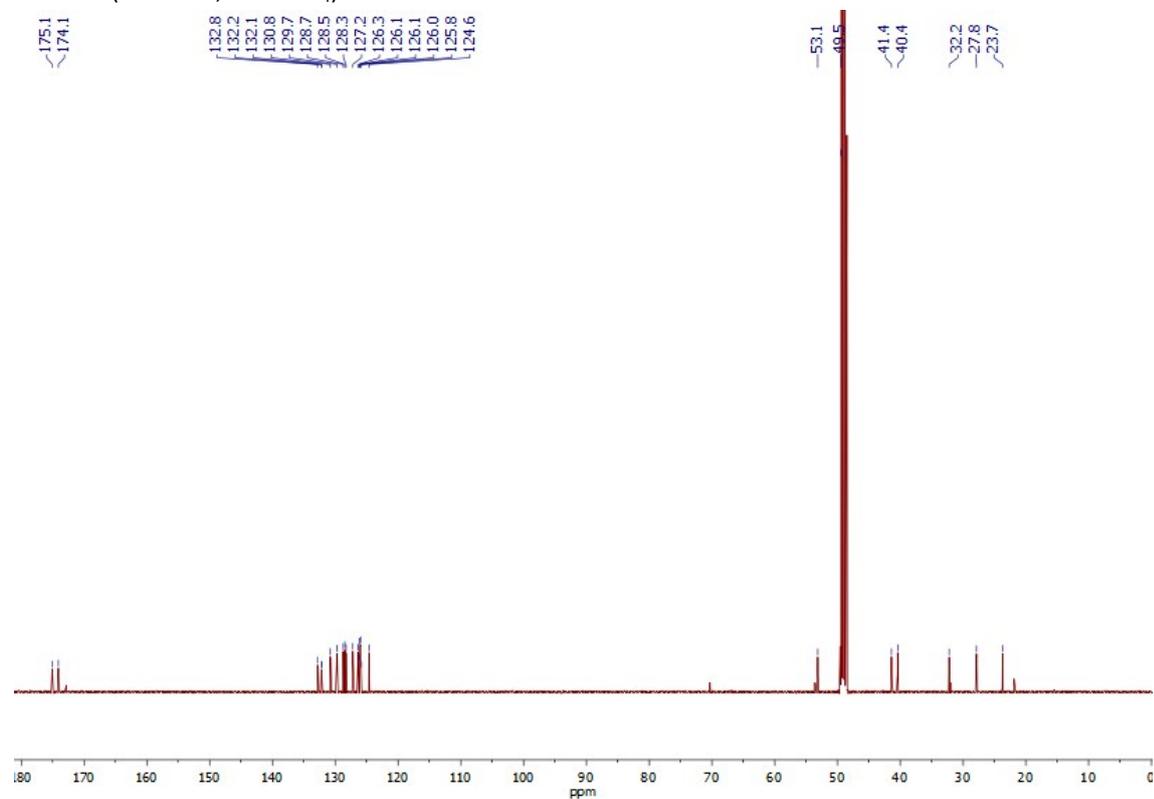


5-Carboxy-5-(2-(pyren-1-yl)acetamido)pentan-1-aminium trifluoroacetate (py-lys)

¹H-NMR (500 MHz, MeOD-d₄)

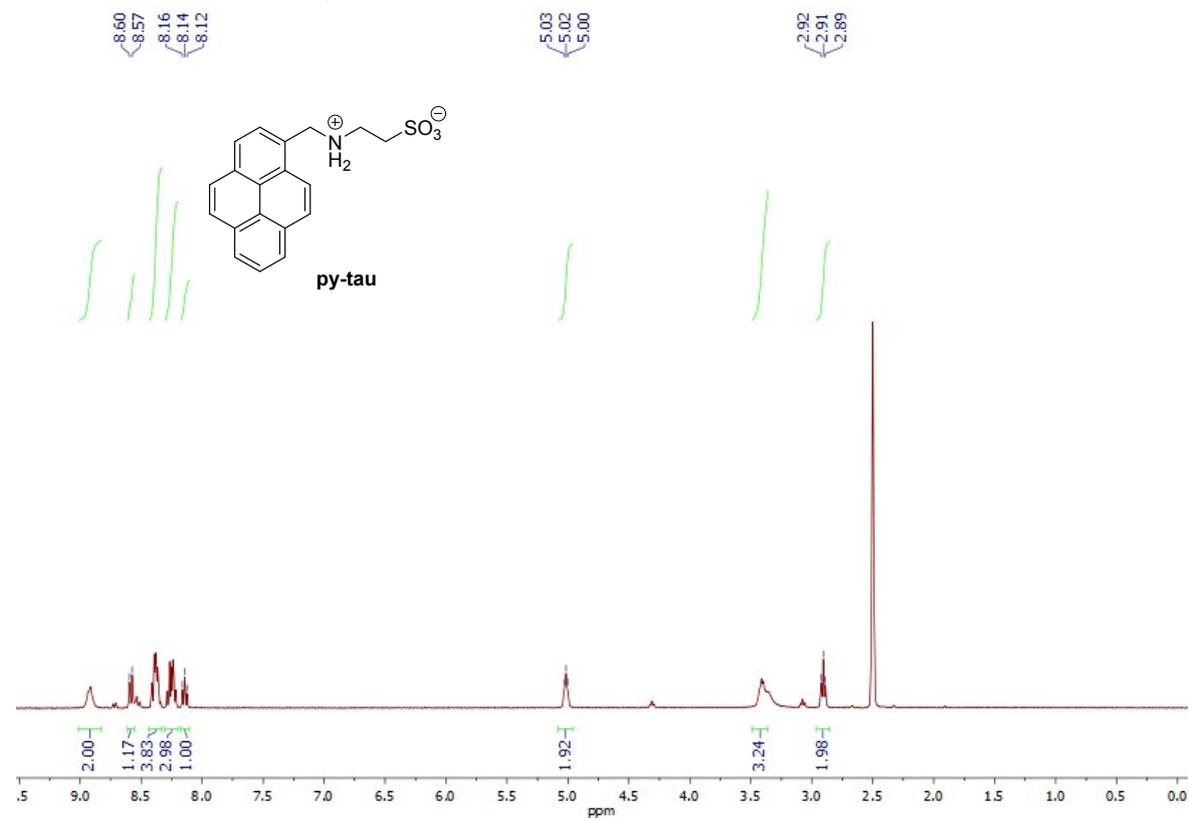


¹³C-NMR (125 MHz, MeOD-d₄)

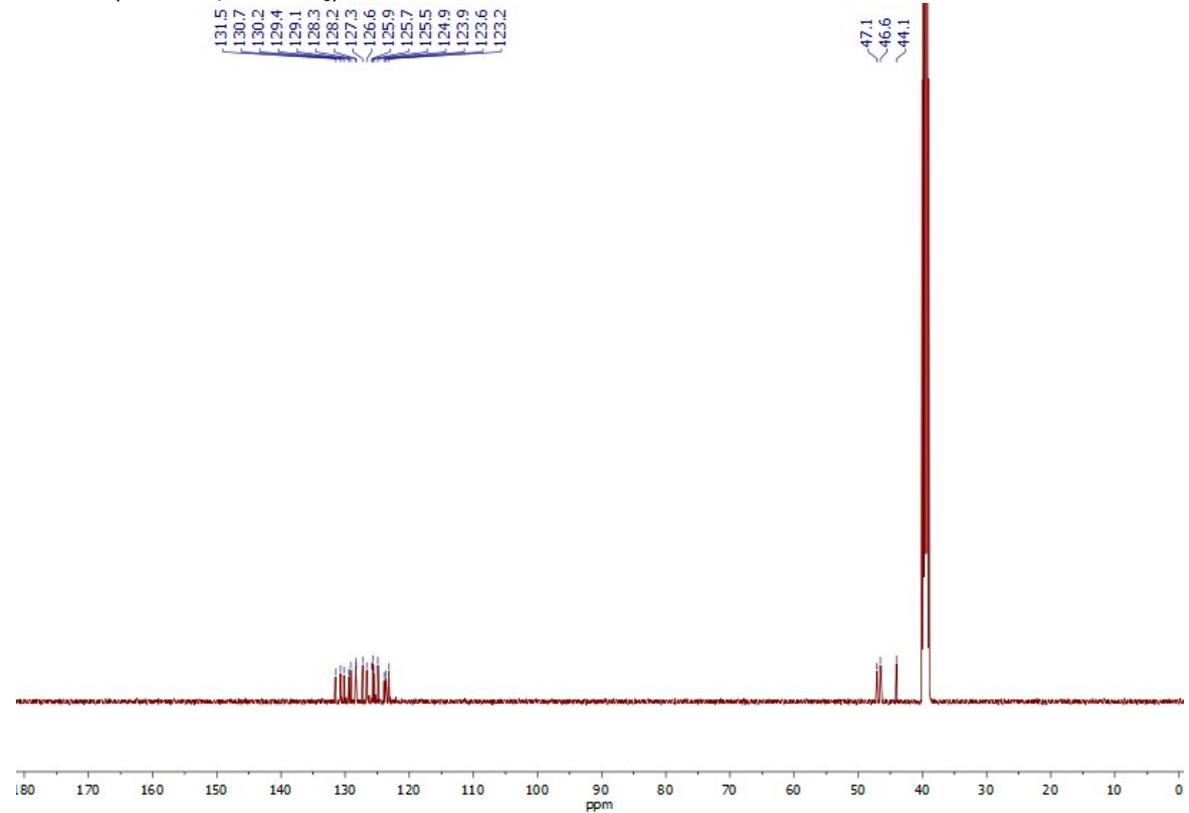


2-((Pyren-1-ylmethyl)ammonio)ethane-1-sulfonate (py-tau)

$^1\text{H-NMR}$ (400 MHz, DMSO-d_6)



$^{13}\text{C-NMR}$ (125 MHz, DMSO-d_6)



S2. AFM Analysis

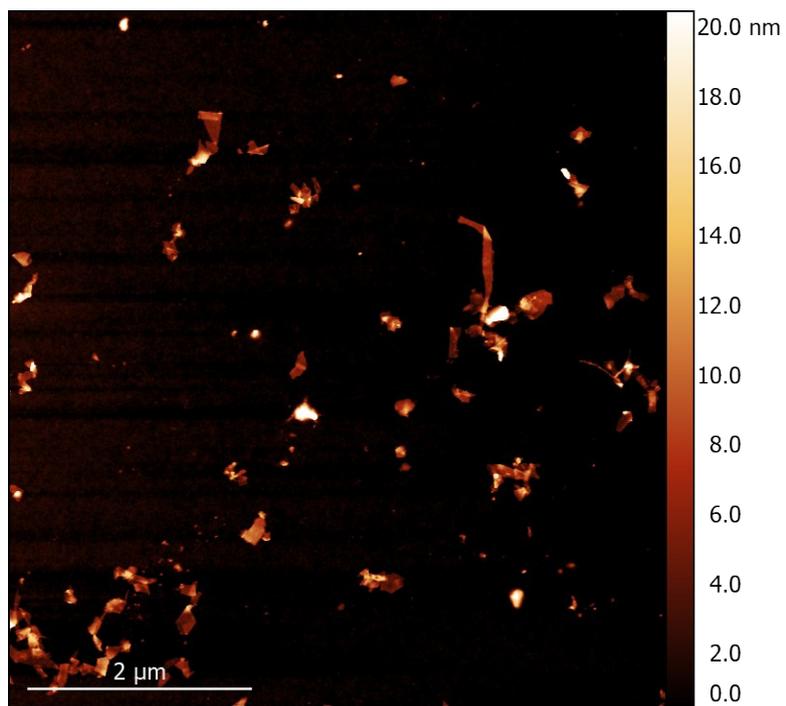


Figure S1 AFM image of graphene flakes prepared with py-lys.

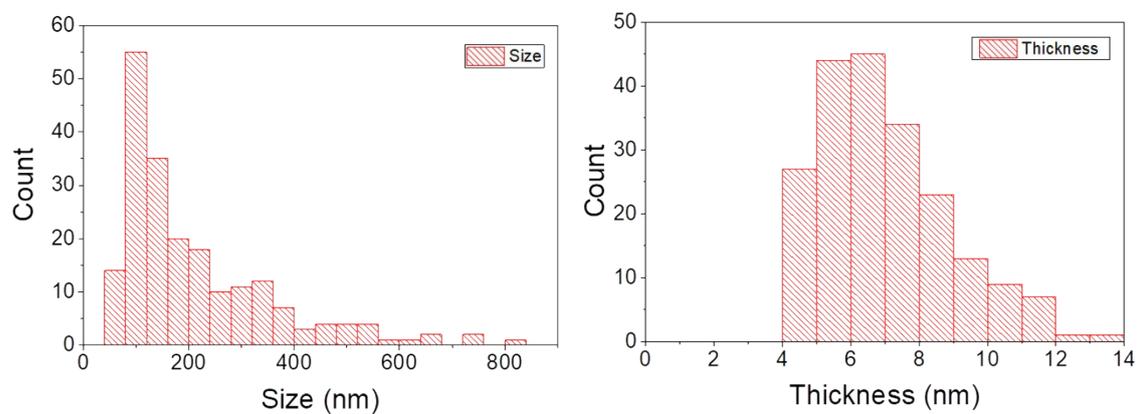


Figure S2 Histograms of AFM statistical analysis of graphene flakes prepared with py-lys.

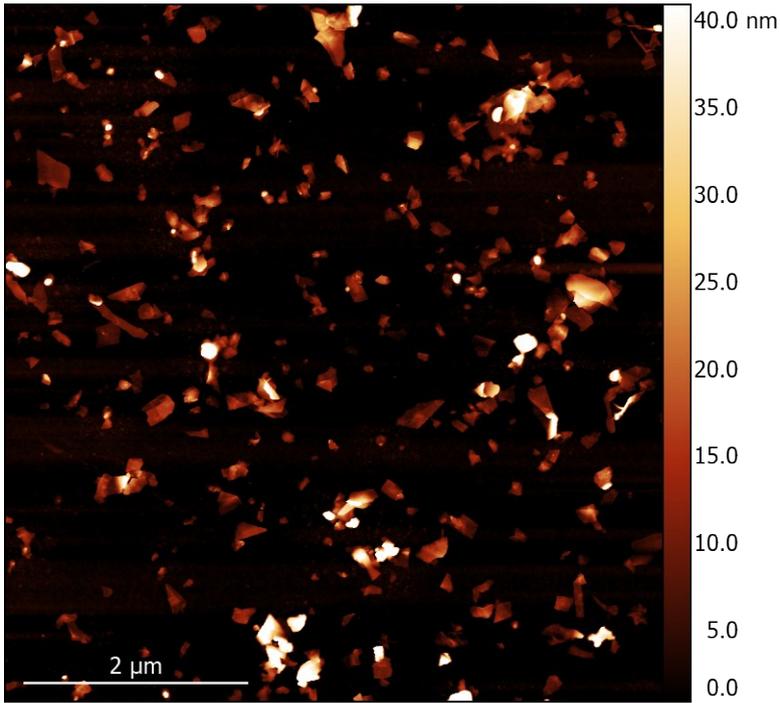


Figure S3 AFM image of graphene flakes prepared with py-tau.

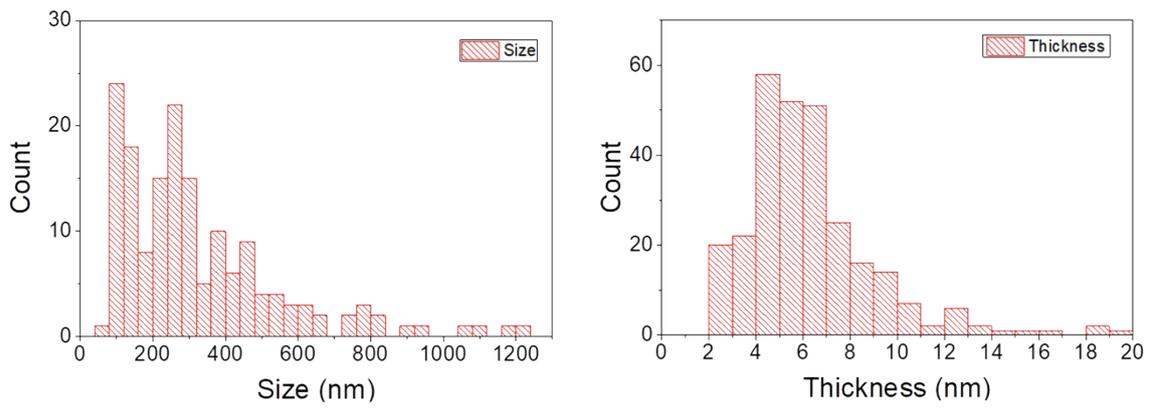


Figure S4 Histograms of AFM statistical analysis of graphene flakes prepared with py-tau.

S3. Raman Analysis

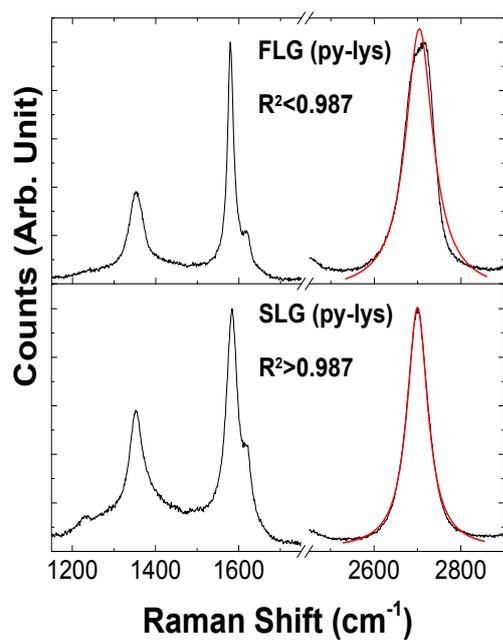
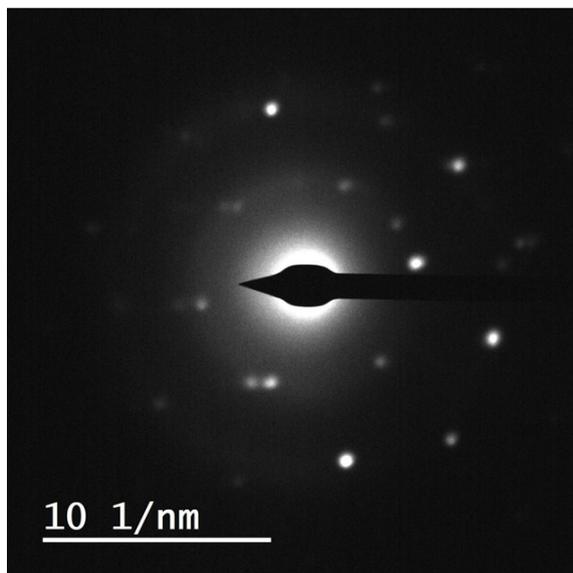
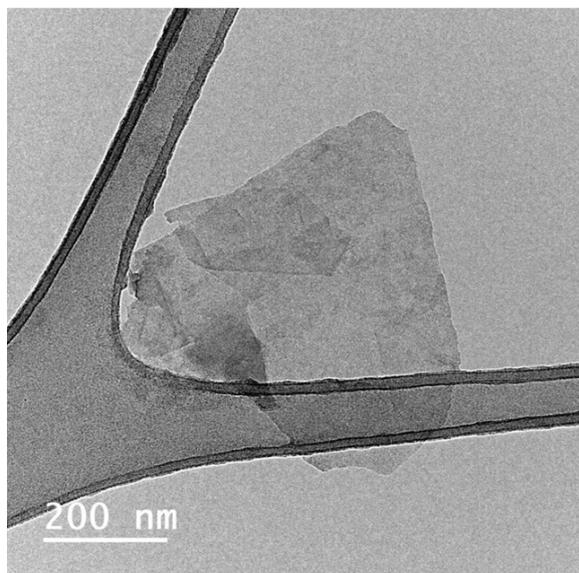
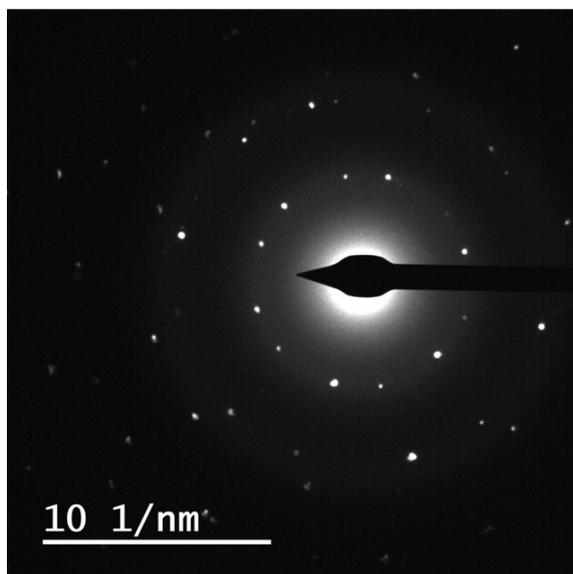
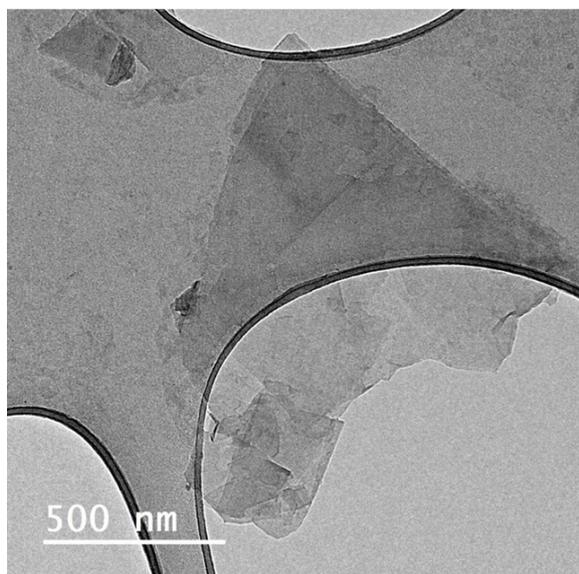
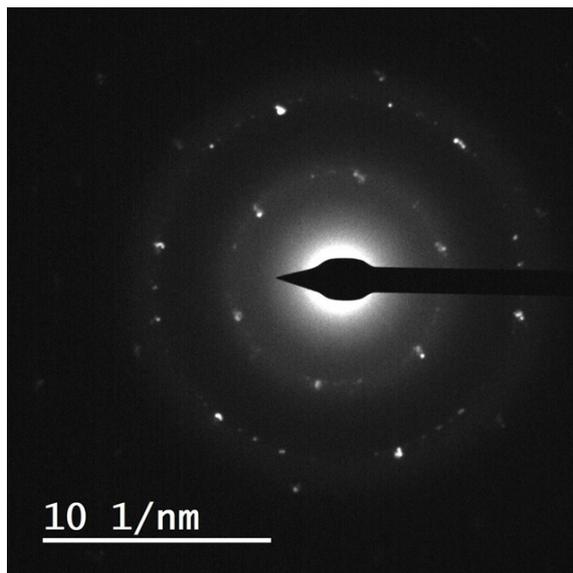
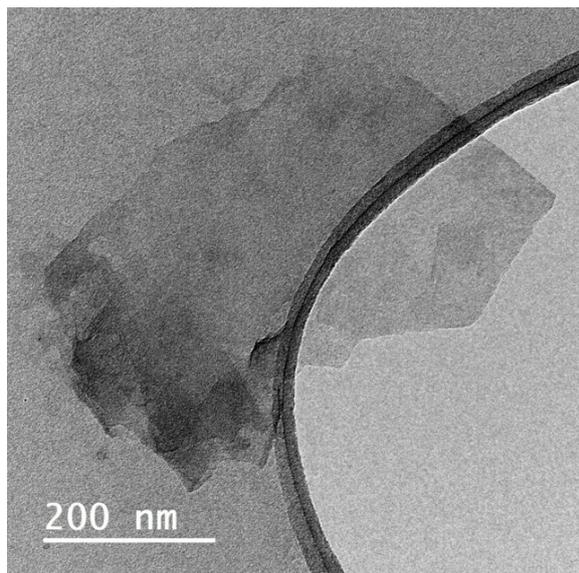


Figure S5 Representative Raman spectra for graphene flakes prepared with py-lys (red curves are the Lorentzian fits of the 2D peaks).

Percentage	Gr/py-lys	Gr/py-tau
Single layer graphene	44%	41.8%
Few-layer graphene	56%	56.4%
Thick Layers	0%	1.8%

Table S1 Qualitative Raman analysis of thickness distribution for graphene dispersions.

S4. TEM images



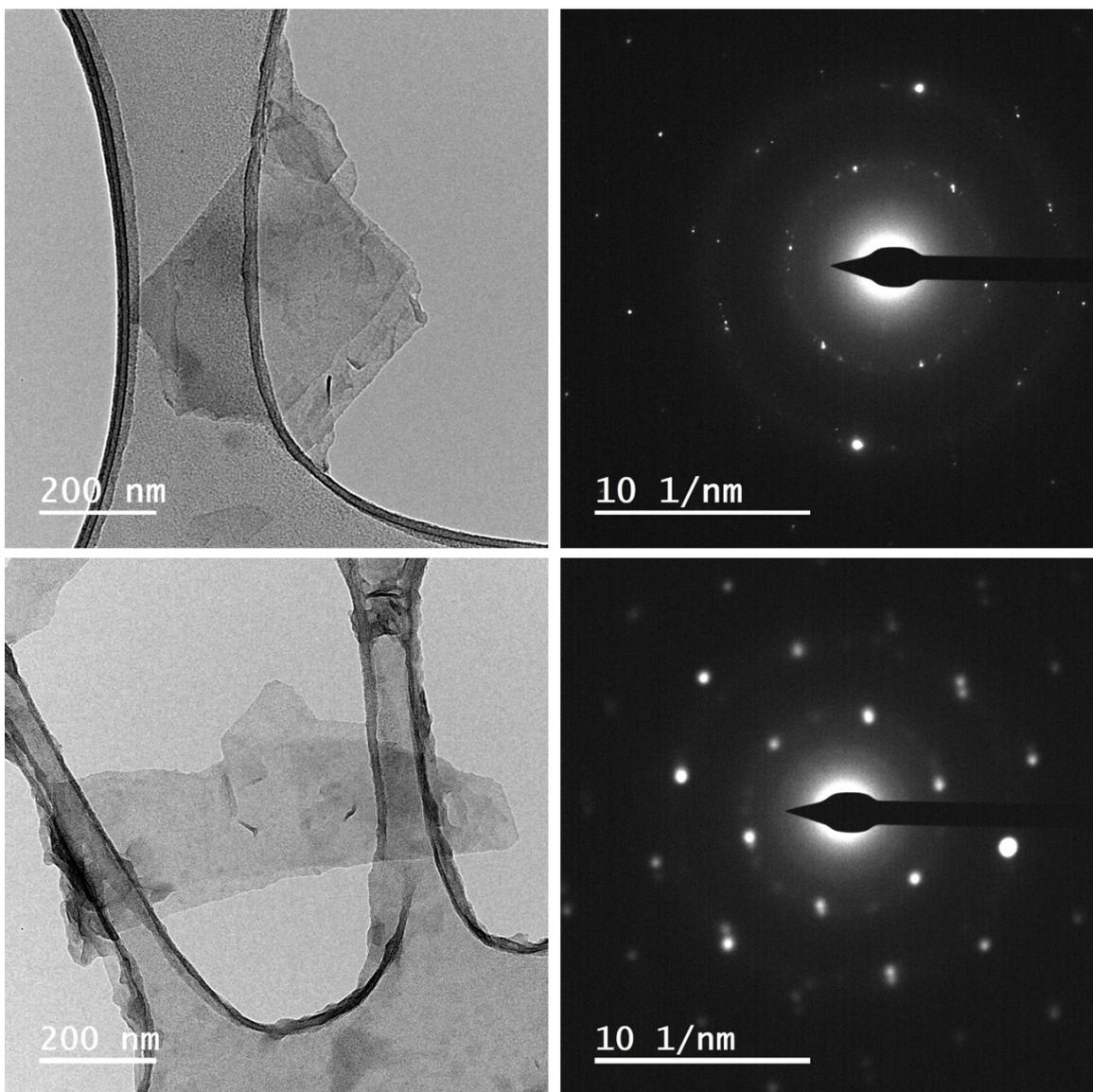


Figure S6 BF-TEM images of individual graphene flakes from Gr/py-lys and corresponding diffraction pattern

S5. Exfoliation of Graphite at Extreme pH

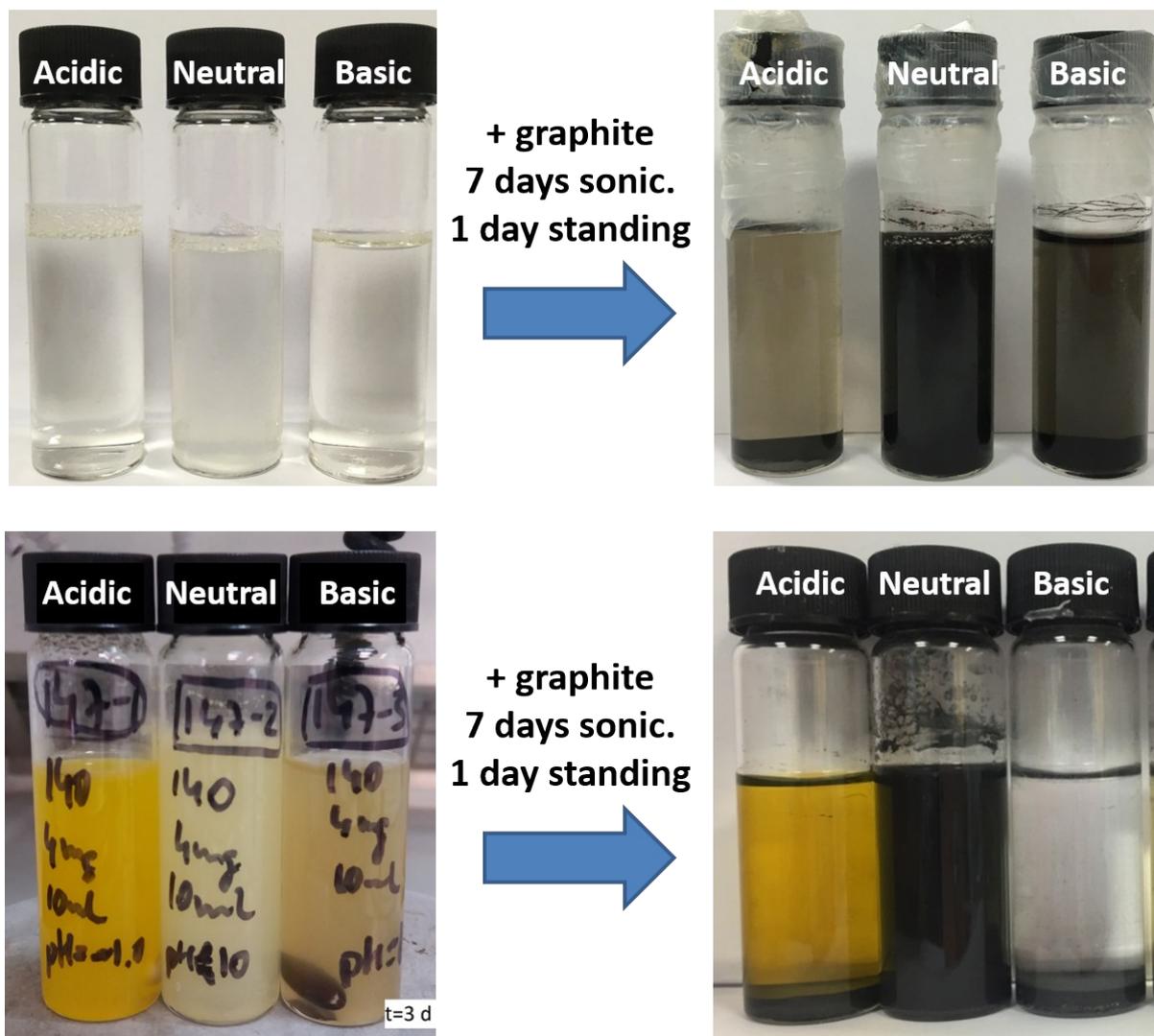


Figure S7 Photograph of (top) py-lys and (bottom) py-tau solution at different pH and the resulting solution after graphite exfoliation for 7 days.