Electronic Supplementary Information for:

Effect of vicinal di-halo substituents on the organogelling properties of aromatic supramolecular gelators and their application as soft template

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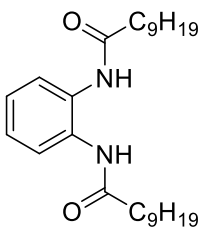
Synthesis and Characterization: The non-halogenated di-amides **2** were prepared by reaction of commercial o-phenylenediamine (Sigma Aldrich, 99.5 %) with the corresponding acid chloride following a standard procedure.[1] The rest of the halogenated compounds were prepared by acylation of the corresponding 4,5-dihalogen-1,2-phenylenediamine with acid chlorides. 4,5-Difluoro-1,2-phenylenediamine and 4,5-dichloro-1,2-phenylenediamine were prepared by nitration of commercial o-difluorobenzene (Sigma Aldrich, 98 %) and o-dichlorobenzene (Sigma Aldrich, 99%) followed by reduction of the nitro groups using the methodology described in literature.[2] 4,5-Dibromo-1,2-phenylenediamine was prepared from o-phenylenediamine using the methodology described in literature.[3] 4,5-Diiodo-1,2-phenylenediamine was prepared from commercial o-dinitrobenzene (Sigma Aldrich, 97%) as described in literature.[4]

General method for the preparation of acid chlorides: To a solution of the carboxylic acid (2,5 mmol) in dichloromethane (1 mL) was added thionyl chloride (0,27 mL; 3,75 mmol). The resulting solution was refluxed overnight (18 h). The unreacted thionyl chloride was removed at atmospheric pressure with nitrogen flow. The resulting product was dissolved in dry acetonitrile (ACN, 5 mL) and used in the acylation step without further treatment.

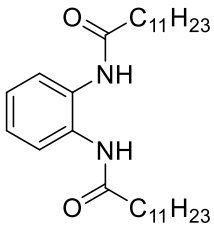
General acylation method: o-Phenylenediamine (1,04 mmol) and triethylamine (2,5 mmol) were dissolved in dried ACN (5 mL), the stirred solution was cooled in an ice bath. The chloride acid solution previously obtained was added dropwise and the reaction was continued for 2 hs at reflux. The solvent was evaporated at vacuum and the solid was suspended in dichloromethane, transferred to a separation funnel and washed with 1% NaOH to eliminate the excess of acid. Unless otherwise indicated, the insoluble solid that remained in the organic phase was filtered, dried under vacuum, and purified as indicated to render the pure final product.

N,N'-(1,2-phenylene)bis(decanamide) (2b): Obtained from 1,2-phenylenediamina and caproic acid

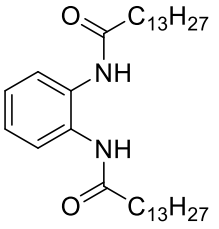


following the general methodology, white solid, recrystallized from n-hexane (53% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.31 (s, 2H), 7.28-7.32 (m, 2H), 7.13-7.16 (m, 2H), 2.30 (t, 4H, *J* = 7.6 Hz), 1.67 (m, 4H), 1.29 (m, 32H), 0.90 (t, 6H, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 172.88, 130.65, 126.00, 125.55, 37.16, 31.88, 29.51, 29.42, 29.34, 29.31, 25.72, 22.67, 14.10. HRMS (ESI): Calc. ($C_{26}H_{45}N_2O_2^+$) 417.34756; Found 417.34641. FT-IR: ν_{max} (cm^{-1}) 3249.65 (NH), 2929.27-2853.40 (C-H), 2384.07-2350.35 (C-N), 1647.78 (C=O).

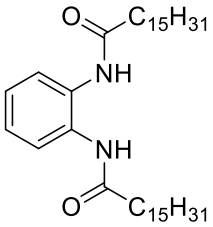
N,N'-(1,2-phenylene)bis(dodecanamide) (2c): Obtained from 1,2-phenylenediamina and lauric acid following the general methodology, white solid, recrystallized from n-hexane (44% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.28 (s, 2H), 7.30-7.32 (m, 2H), 7.14-7.16 (m, 2H), 2.30 (t, 4H, *J* = 7.7 Hz), 1.67 (m, 4H), 1.28 (m, 32H), 0.89 (t, 6H, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 172.86, 130.64, 126.02, 125.54, 37.17, 31.91, 29.66, 29.64, 29.56, 29.42, 29.35, 29.34, 25.73, 22.68, 14.11. HRMS (ESI): Calc. ($C_{30}H_{52}N_2O_2$+Na^+) 495.3921; Found 495.3925. FT-IR: ν_{max} (cm^{-1}) 3234.67 (NH), 2919.53-2852.90 (C-H), 2361.28-2343.28 (C-N), 1644.57 (C=O).



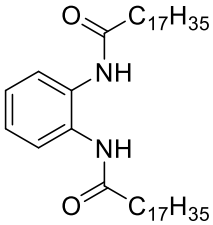
N,N'-(1,2-phenylene)ditetradecanamide (2d): Obtained from 1,2-phenylenediamina and myristic acid following the general methodology, white solid, recrystallized from n-hexane (55% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.34 (s, 2H), 7.29-7.32 (m, 2H), 7.13-7.17 (m, 2H), 2.30 (t, 4H, *J* = 7.6 Hz), 1.67 (m, 4H), 1.28 (m, 32H), 0.89 (t, 6H, *J* = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 172.86, 130.65, 126.02, 125.55, 37.18, 31.92, 29.70, 29.67, 29.56, 29.42, 29.36, 29.34, 25.73, 22.69, 14.11. HRMS (ESI): Calc. ($C_{34}H_{61}N_2O_2^+$) 529.47276; Found 529.47531. FT-IR: ν_{max} (cm^{-1}) 3232.79 (NH), 2918.03-2853.40 (C-H), 2384.07-2350.35 (C-N), 1647.78 (C=O).



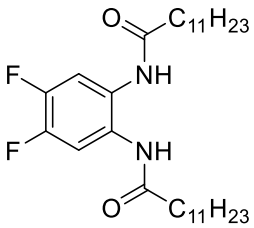
N,N'-(1,2-phenylene)dipalmitamide (2e): Obtained from 1,2-phenylenediamina and palmitic acid following the general methodology, white solid, recrystallized from methanol (50% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.15 (s, 2H), 7.33-7.36 (m, 2H), 7.16-7.19 (m, 2H), 2.33 (t, 4H, *J* = 7.6 Hz), 1.69 (m, 4H), 1.27 (m, 48H), 0.89 (t, 6H, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 172.72, 130.60, 126.12, 125.50, 37.26, 31.93, 29.71, 29.67, 29.56, 29.42, 29.37, 29.33, 25.76, 22.69, 14.12. HRMS (ESI): Calc. ($C_{38}H_{69}N_2O_2$) 585.5354; Found 585.5383. FT-IR: ν_{max} (cm^{-1}) 3236.02 (NH), 2919.30-2851.55 (C-H), 2361.51-2342.60 (C-N), 1646.15 (C=O).



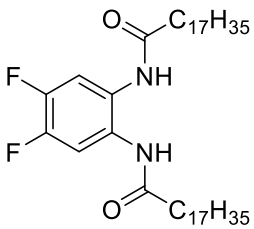
N,N'-(1,2-phenylene)distearamide (2f): Obtained from 1,2-phenylenediamina and stearic acid following the general methodology, white solid, recrystallized from methanol (42% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.20 (s, 2H), 7.32-7.34 (m, 2H), 7.15-7.17 (m, 2H), 2.32 (t, 4H, *J* = 7.7 Hz), 1.68 (m, 4H), 1.27 (m, 56H), 0.89 (t, 6H, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 172.78, 130.62, 126.08, 125.52, 37.22, 31.92, 29.72, 29.68, 29.67, 29.57, 29.43, 29.37, 29.34, 25.75, 22.69, 14.12. HRMS (ESI): Calc. ($C_{42}H_{76}N_2O_2$+Na^+) 663.5799; Found 663.5784. FT-IR: ν_{max} (cm^{-1}) 3234.22 (NH), 2918.18-2850.87 (C-H), 2360.72-2341.70 (C-N), 1648.17 (C=O).



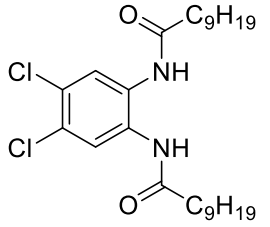
N,N'-(4,5-difluoro-1,2-phenylene)didodecanamide (3c): Obtained from 4,5-difluoro-1,2-phenylenediamina and lauric acid following the general methodology, white solid, purified by column chromatography silicagel, n-hexane:ethyl acetate 9:1 (68% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.12 (s, 2H), 7.20 (t, 2H, *J* = 9.5 Hz), 2.33 (t, 4H, *J* = 7.6 Hz), 1,68 (m, 4H), 1,28 (m, 32H), 0,89 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 173.10, 145.98, 126.97, 114.04, 37.00, 31.91, 29.64, 29.63, 29.51, 29.35, 29.28, 25.60, 22.68, 14.10. HRMS (ESI): Calc. ($C_{30}H_{50}F_2N_2O_2$+Na^+) 531.3733; Found 531.3715. FT-IR: ν_{max} (cm^{-1}) 3258.08 (NH), 2926.46-2853.40 (C-H), 2358.78-2339.11 (C-N), 1647.78 (C=O).



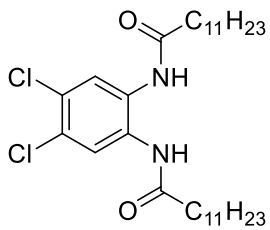
N,N'-(4,5-difluoro-1,2-phenylene)distereamide (3f): Obtained from 4,5-difluoro-1,2-phenylenediamine and stearic acid following the general methodology, white solid recrystallized from methanol (43% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.08 (s, 2H), 7.23 (t, 2H, *J* = 9.5 Hz), 2.34 (t, 4H, *J* = 7.6 Hz), 1,69 (m, 4H), 1,27 (m, 56H), 0,89 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 172.87, 146.57, 126.90, 114.02, 37.10, 31.92, 29.71, 29.68, 29.66, 29.52, 29.36, 29.27, 25.64, 22.68, 14.15. HRMS (ESI): Calc. ($C_{42}H_{74}F_2N_2O_2$+Na^+) 699.5611; Found 699.5617. FT-IR: ν_{max} (cm^{-1}) 3244.03 (NH), 2918.03-2847.78 (C-H), 2364.40-2347.54 (C-N), 1647.78 (C=O).



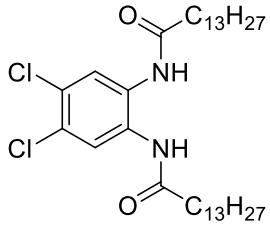
N,N'-(4,5-dichloro-1,2-phenylene)bis(decanamide) (4b): Obtained from 4,5-dichloro-1,2-phenylenediamine and capric acid following the general methodology, white solid recrystallized from methanol (20% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.31 (s, 2H), 7.43 (s, 2H), 2.32 (t, 4H, *J* = 7.7 Hz), 1,68 (m, 4H), 1,29 (m, 24H), 0,90 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 173.28, 130.05, 129.30, 126.68, 36.99, 31.87, 29.46, 29.35, 29.29, 29.26, 25.49, 22.67, 14.10. HRMS (ESI): Calc. ($C_{26}H_{42}Cl_2N_2O_2$+Na^+) 507.2516; Found 507.2496. FT-IR: ν_{max} (cm^{-1}) 3248.62 (NH), 2922.45-2851.55 (C-H), 2359.93-2342.60 (C-N), 1646.15 (C=O).



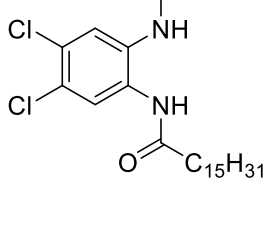
N,N'-(4,5-Dichloro-1,2-phenylene)didodecanamide (4c): Obtained from 4,5-dichloro-1,2-phenylenediamine and lauric acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 9:1, white solid (65% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.35 (s, 2H), 7.41 (s, 2H), 2.31 (t, 4H, *J* = 7.9 Hz), 1,67 (m, 4H), 1,28 (m, 32H), 0,89 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 173.21, 130.04, 129.30, 126.64, 37.03, 31.92, 29.65, 29.63, 29.52, 29.36, 29.27, 29.22, 25.52, 22.68, 14.10. HRMS (ESI): Calc. ($C_{30}H_{51}Cl_2N_2O_2$+Na^+) 541.3322; Found 541.3318. FT-IR: ν_{max} (cm^{-1}) 3252.46 (NH), 2920.84-2850.59 (C-H), 2361.59-2344.73 (C-N), 1647.78 (C=O).



N,N'-(4,5-dichloro-1,2-phenylene)ditetracanamide (4d): Obtained from 4,5-dichloro-1,2-phenylenediamine and myristic acid following the general methodology, white solid recrystallized from methanol (24% yield). ^{1}H NMR ($CDCl_3$, 500MHz): δ(ppm) 8.36 (s, 2H), 7.41 (s, 2H), 2.32 (t, 4H, *J* = 7.7 Hz), 1.67 (m, 4H), 1.28 (m, 40H), 0.89 (t, 6H, *J* = 6.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 173.38, 130.07, 129.31, 126.74, 36.97, 31.93, 29.71, 29.68, 29.67, 29.65, 29.52, 29.37, 29.28, 25.49, 22.69, 14.11. HRMS (ESI): Calc. ($C_{34}H_{59}Cl_2N_2O_2$) 597.3948; Found 597.3948. FT-IR: ν_{max} (cm^{-1}) 3232.86 (NH), 2920.88-2849.97 (C-H), 2361.51-2342.60 (C-N), 1649.30 (C=O).



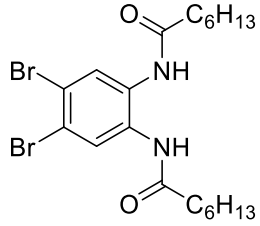
N,N'-(4,5-dichloro-1,2-phenylene)dipalmitamide (4e): Obtained from 4,5-dichloro-1,2-phenylenediamine and palmitic acid following the general methodology, white solid recrystallized from methanol (20% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.31 (s, 2H), 7.43 (s, 2H), 2.32 (t, 4H, *J* = 7.6 Hz), 1.67 (m, 4H), 1.27 (m, 48H), 0.89 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 173.27, 130.05, 129.31, 126.67, 36.99, 31.93, 29.71, 29.69, 29.66, 29.53, 29.37, 29.27, 25.50, 22.69, 14.12. HRMS (ESI): Calc. ($C_{38}H_{67}Cl_2N_2O_2$) 653.4574; Found 653.4570. FT-IR: ν_{max} (cm^{-1}) 3262.80 (NH), 2919.30-2851.55 (C-H), 2361.51-2344.18 (C-N), 1649.30 (C=O).



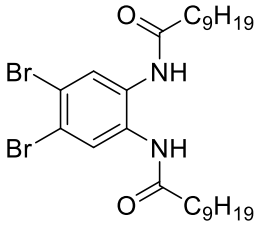
N,N'-(4,5-dichloro-1,2-phenylene)distearamide (4f): Obtained from 4,5-dichloro-1,2-phenylenediamine and stearic acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 9:1, white solid (65% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.19 (s, 2H), 7.47 (s, 2H), 2.33 (t, 4H, *J* = 7.6 Hz), 1.69 (m, 4H), 1.27 (m, 56H), 0.89 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 173.10, 130.01, 129.38, 126.64, 37.03, 31.93, 29.72, 29.67,

29.53, 29.37, 29.26, 25.53, 22.70, 14.12. HRMS (ESI): Calc. ($C_{42}H_{75}Cl_2N_2O_2^+$) 709.5200; Found 709.5211. FT-IR: ν_{max} (cm^{-1}) 3263.70 (NH), 2918.03-2853.40 (C-H), 2364.40-2341.92 (C-N), 1734.89 (C=O).

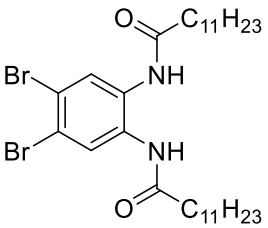
N,N'-(4,5-dichloro-1,2-phenylene)diheptanamide (5a): Hepnanoic acid (0.14 ml, 0.95 mmol) was added to a suspension of DCC (233.4mg, 1.06 mmol) in dichloromethane (10 mL) at room temperature. After 10 min 4,5-dibromo-1,2-phenylenediamine (100 mg; 0,38 mmol) was added and the reaction was kept at room temperature overnight. The mixture was filtered and the dichloromethane evaporated at vacuum. The solid was purified by column chromathography (silicagel, n-hexane/ethyl acetate 8:2). Compound 5a was obtained as a white solid (32 % yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.39 (s, 2H), 7.56 (s, 2H), 2.32 (t, 4H, *J* = 7.5 Hz), 1.68 (m, 4H), 1.35 (m, 12H), 0.92 (t, 6H, *J* = 6.2 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 173.42, 130.73, 129.80, 120.99, 36.99, 31.53, 28.94, 25.41, 22.51, 14.05. HRMS (ESI): Calc. ($C_{20}H_{30}Br_2N_2O_2$+Na^+) 511.0566; Found 511.0567. FT-IR: ν_{max} (cm^{-1}) 3204.92 (NH), 2921.55-2851.77 (C-H), 2365.56-2316.65 (C-N), 1637.59 (C=O).



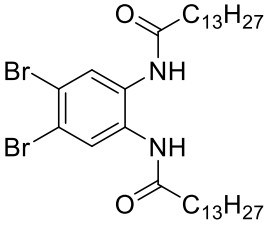
N,N'-(4,5-dibromo-1,2-phenylene)bis(decanamide) (5b): Obtained from 4,5-dibromo-1,2-phenylenediamine and capric acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 9:1, yellow solid (52% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.38 (s, 2H), 7.56 (s, 2H), 2.32 (t, 4H, *J* = 7.6 Hz), 1,68 (m, 4H), 1,29 (m, 24H), 0,90 (t, 6H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 173.42, 130.74, 129.81, 120.98, 37.00, 31.88, 29.47, 29.37, 29.30, 29.28, 25.46, 22.68, 14.11. HRMS (ESI): Calc. ($C_{26}H_{43}Br_2N_2O_2^+$) 573.16858; Found 573.16881. FT-IR: ν_{max} (cm^{-1}) 3215.93 (NH), 2920.84-2853.40 (C-H), 2364.40-2347.54 (C-N), 1639.34 (C=O).



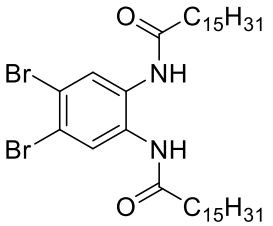
N,N'-(4,5-dibromo-1,2-phenylene)didodecanamide (5c): Obtained from 4,5-dichloro-1,2-phenylenediamine and lauric acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 8:2, light yellow solid (46% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.47 (s, 2H), 7.54 (s, 2H), 2.31 (t, 4H, *J* = 7.7 Hz), 1.67 (m, 4H), 1.28 (m, 32H), 0.89 (t, 6H, *J* = 7.1 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 173.49, 130.74, 129.79, 120.93, 36.92, 31.92, 29.65, 29.63, 29.52, 29.38, 29.35, 29.28, 25.44, 22.69, 14.12. HRMS (ESI): Calc. ($C_{30}H_{50}Br_2N_2O_2$+Na^+) 651.2131; Found 651.2131. FT-IR: ν_{max} (cm^{-1}) 3216.63 (NH), 2921.55-2851.32 (C-H), 2359.48-2342.82 (C-N), 1647.54 (C=O).



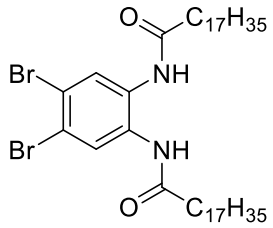
N,N'-(4,5-dibromo-1,2-phenylene)ditetradecanamide (5d): Obtained from 4,5-dichloro-1,2-phenylenediamine and myristic acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 9:1, light yellow solid (65% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 8.36 (s, 2H), 7.57 (s, 2H), 2.32 (t, 4H, *J* = 7.6 Hz), 1.67 (m, 4H), 1.27 (m, 40H), 0.89 (t, 6H, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 173.54, 130.75, 129.81, 120.94, 36.90, 31.92, 29.71, 29.67, 29.53, 29.37, 29.28, 25.44, 22.69, 14.11. HRMS (ESI): Calc. ($C_{34}H_{58}Br_2N_2O_2$+Na^+) 707.2757; Found 707.2760. FT-IR: ν_{max} (cm^{-1}) 3208.33 (NH), 2355.17 (C-N), 1648.40 (C=O).



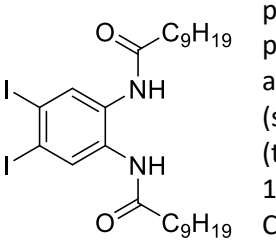
N,N'-(4,5-dibromo-1,2-phenylene)dipalmitamide (5e): Obtained from 4,5-dibromo-1,2-phenylenediamine and palmitic acid following the general methodology, white solid recrystallized from methanol (55% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 8.37 (s, 2H), 7.56 (s, 2H), 2.32 (t, 4H, *J* = 7.7 Hz), 1.68 (m, 4H), 1.27 (m, 48H), 0.89 (t, 6H, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 173.39, 130.73, 129.77, 120.99, 36.97, 31.93, 29.72, 29.69, 29.67, 29.53, 29.37, 29.28, 25.46, 22.69, 14.12. HRMS (ESI): Calc. ($C_{38}H_{66}Br_2N_2O_2$+Na^+) 763.3383; Found 763.3350. FT-IR: ν_{max} (cm^{-1}) 3207.88 (NH), 2916.71-2850.87 (C-H), 2359.26-2340.24 (C-N), 1648.17 (C=O).



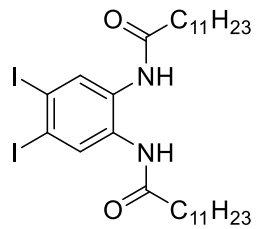
N,N'-(4,5-dibromo-1,2-phenylene)distearamide (5f): Obtained from 4,5-dichloro-1,2-phenylenediamine and stearic acid following the general methodology, white solid recrystallized from acetone (53% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.27 (s, 2H), 7.60 (s, 2H), 2.33 (t, 4H, *J* = 7.6 Hz), 1.68 (m, 4H), 1.27 (m, 56H), 0.89 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$ /1%CD_3OD, 125 MHz): δ(ppm) 173.04, 130.61, 129.46, 120.91, 37.00, 31.88, 29.66, 29.64, 29.61, 29.49, 29.33, 29.32, 29.22, 25.55, 22.64, 14.06. HRMS (ESI): Calc. ($C_{42}H_{74}Br_2N_2O_2$+Na^+) 819.4009; Found 819.3998. FT-IR: ν_{max} (cm^{-1}) 3197.64 (NH), 2918.18-2852.34 (C-H), 2360.72-2343.16 (C-N), 1648.17 (C=O).



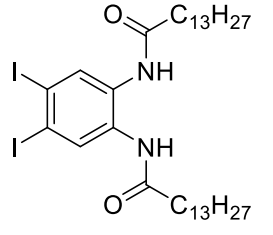
N,N'-(4,5-diiodo-1,2-phenylene)bis(decanamide) (6b): Obtained from 4,5-diiodo-1,2-phenylenediamine and capric acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 9:1, yellow solid (37% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.35 (s, 2H), 7.75 (s, 2H), 2.33 (t, 4H, *J* = 7.8 Hz), 1.69 (m, 4H), 1.29 (m, 24H), 0.90 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 173.36, 135.40, 131.40, 103.19, 37.06, 31.89, 29.48, 29.40, 29.31, 25.48, 22.69, 14.12. HRMS (ESI): Calc. ($C_{26}H_{43}I_2N_2O_2^+$) 669.14084; Found 669.14288. FT-IR: ν_{max} (cm^{-1}) 3215.93 (NH), 2920.84-2856.21 (C-H), 2361.59-2341.92 (C-N), 1737.70 (C=O).



N,N'-(4,5-diiodo-1,2-phenylene)bis(dodecanamide) (6c): Obtained from 4,5-diiodo-1,2-phenylenediamine and lauric acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 8:2, yellow solid (70% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.35 (s, 2H), 7.75 (s, 2H), 2.33 (t, 4H, *J* = 7.7 Hz), 1.68 (m, 4H), 1.28 (m, 32H), 0.89 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 173.35, 135.38, 131.38, 103.19, 37.06, 31.92, 29.66, 29.64, 29.53, 29.41, 29.36, 29.31, 25.49, 22.69, 14.12. HRMS (ESI): Calc. ($C_{30}H_{51}I_2N_2O_2^+$) 725.2034; Found 725.2012. FT-IR: ν_{max} (cm^{-1}) 3218.74 (NH), 2923.65-2853.40 (C-H), 2361.59-2341.92 (C-N), 1647.78 (C=O).

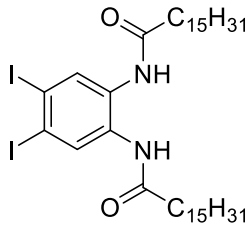


N,N'-(4,5-diiodo-1,2-phenylene)bis(tetradecanamide) (6d): Obtained from 4,5-diiodo-1,2-phenylenediamine and myristic acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 8:2, yellow solid (46% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.35 (s, 2H), 7.75 (s, 2H), 2.32 (t, 4H, *J* = 7.7 Hz), 1.68 (m, 4H), 1.27 (m, 40H), 0.89 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ(ppm) 173.37, 135.39, 131.38, 103.18, 37.06, 31.93, 29.72, 29.70, 29.67,

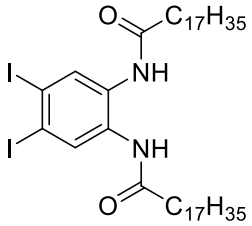


29.54, 29.41, 29.37, 29.31, 25.48, 22.70, 14.13. HRMS (ESI): Calc. ($C_{34}H_{59}I_2N_2O_2^+$) 781.26604; Found 781.26559. FT-IR: ν_{max} (cm^{-1}) 3215.93 (NH), 2920.84-2853.40 (C-H), 2364.40-2344.73 (C-N), 1647.78 (C=O).

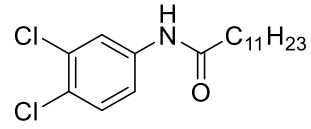
N,N'-(4,5-Diiodo-1,2-phenylene)dipalmitamide (6e): Obtained from 4,5-diiodo-1,2-phenylenediamine and palmitic acid following the general methodology, white solid recrystalized from hexane (39% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 8.25 (s, 2H), 7.80 (s, 2H), 2.33 (t, 4H, *J* = 7.6 Hz), 1.69 (m, 4H), 1.27 (m, 48H), 0.89 (t, 6H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$/1% CD_3OD, 125 MHz): δ(ppm) 173.21, 134.91, 131.16, 102.77, 36.80, 31.72, 29.50, 29.46, 29.34, 29.20, 29.16, 29.08, 25.49, 22.48, 13.84. HRMS (ESI): Calc. ($C_{38}H_{67}I_2N_2O_2^+$) 837.3287; Found 837.3264. FT-IR: ν_{max} (cm^{-1}) 3369.95 (NH), 2919.30-2853.12 (C-H), 2361.51-2342.60 (C-N), 1649.30 (C=O).



N,N'-(4,5-diiodo-1,2-phenylene)distearamide (6f): Obtained from 4,5-diiodo-1,2-phenylenediamine and stearic acid following the general methodology, white solid recrystalized from hexane (12% yield). ^{1}H NMR ($CDCl_3$/MeOD, 500 MHz): δ(ppm) 7.86 (s, 2H), 2.29 (t, 4H, *J* = 7.6 Hz), 1.63 (m, 4H), 1.20 (m, 56H), 0.83 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$/1% CD_3OD, 125 MHz): δ(ppm) 173.13, 135.02, 131.27, 102.90, 36.89, 31.79, 29.57, 29.53, 29.41, 29.26, 29.23, 29.14, 25.54, 22.55, 13.93. HRMS (ESI): Calc. ($C_{42}H_{74}I_2N_2O_2$+Na^+) 915.3732; Found 915.3718. FT-IR: ν_{max} (cm^{-1}) 3362.06 (NH), 2920.84-2850.59 (C-H), 2361.59-2341.92 (C-N), 1740.52 (C=O).



N-(3,4-Dichlorophenyl)dodecanamide (7): Obtained from commercial 3,4-dichloroaniline and Lauric acid following the general methodology, the product was purified by column chromatography on silicagel, n-hexane:ethyl acetate 9:1, white solid (20% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 7.76 (s, 1H), 7.45-7.47 (m, 1H), 7.34 (s, 2H), 2.35 (t, 2H, *J = 7.9Hz*), 1.71 (m, 2H), 1.26 (m, 16H), 0.88 (t, 3H, *J = 6.9Hz*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ(ppm) 171.71, 137.39, 132.70, 130.42, 127.30, 121.49, 118.99, 37.68, 31.88, 29.58, 29.44, 29.33, 29.30, 29.21, 25.47, 22.66, 14.09. HRMS (ESI): Calc. 366,1362 ($C_{18}H_{27}Cl_2NO$+Na^+); Found. 366.1369. FT-IR: ν_{max} (cm^{-1}) 3311.20 (NH), 2922.23-2851.32 (C-H), 2359.03-2342.82 (C-N), 1670.23 (C=O).



Gelling ability

The gelling ability of all compounds was studied using the inverted tube method in 34 solvents. All solvents tested are listed in table S3. If a solvent does not appear in a table it could not be gelled by any compound. Since the molecular weights of the halogens vary widely, in order to be able to compare the gelling ability based on the CCG the values are expressed in mM.

Table S1. Gelation properties and critical concentration for gelation of non-halogenated (**2b-f**) and fluorinated compounds (**3c,f**).[a]

Solvent	2b	2c	2d	2e	2f	3c	3f
Ethyl ether	P	P	P	P	P	P	P
Dichloromethane	S	S	S	P	P	P	P
Acetone	P	P	P	P	P	P	P
Chloroform	S	S	S	P	P	S	P
Methanol	P	P	P	P	P	P	P
THF	S	S	S	P	S	S	P
Isopropyl ether	P	P	P	P	P	P	P
***n*-Hexane**	G (30.0)	P	G (31.5)	P	P	P	OG (18.8)
Ethyl acetate	P	P	P	P	P	P	P
CCl_4	P	S	P	P	S	P	P
Ethanol	P	P	P	P	P	P	P
Methylethylketone	S	P	P	P	P	P	P
Cyclohexane	G (120)	P	P	P	OG (26.0)	P	P
Acetonitrile	P	P	P	P	P	P	P
2-Propanol	S	P	P	P	P	P	P
1,2-Dichloroethane	S	P	P	P	P	P	OG (36.9)
1-Propanol	P	P	P	P	P	P	P
Water	I	I	I	I	I	I	I
DMSO	S	OG (26.4)	OG (31.5)	OG (28.5)	OG (19.5)	OG (24.6)	OG (73.8)
1-Octanol	P	P	P	P	OG (39.0)	P	OG (74.0)

[a] The values in parentheses are CCG (mM). Inverted tube test code G: transparent gel, OG: opaque gel, S: Soluble, I: Insoluble, S: soluble, P: soluble after heating but precipitate upon cooling.

Table S2. Gelation properties and critical concentration for gelation (CCG) of chlorinated compounds.[a]

Solvent	4b	4c	4d	4e	4f
Ethyl ether	P	P	P	P	P
dichloromethane	S	P	OG (41.8)	P	P
Acetone	P	P	OG (27.9)	P	G (35.2)
Chloroform	P	S	P	S	P
Methanol	P	P	P	P	P
THF	S	S	P	P	P
Isopropyl ether	P	P	P	OG (76.5)	P
***n*-Hexane**	P	P	P	P	P
Ethyl acetate	P	P	P	OG (76.5)	P
CCl_4	P	P	P	P	P
Ethanol	OG (34.3)	OG (18.5)	G (20.8)	OG (76.5)	P
Methylethylketone	P	G (30.8)	OG (83.6)	OG (76.5)	OG (70.4)
Cyclohexane	P	P	P	P	OG (70.4)
Acetonitrile	OG (51.5)	G (1.85)	OG (41.8)	P	I
2-Propanol	G (51.5)	OG (46.3)	G (83.6)	P	OG (23.5)
1,2-Dichloroethane	OG (103)	OG (30.8)	P	P	OG (70.4)
1-Propanol	G (51.5)	P	OG (83.6)	P	OG (23.5)
***n*-Heptane**	P	OG (92.5)	OG (83.6)	P	OG (70.4)
Water	I	I	I	I	I
Methylisobutylketone	S	G (46.3)	P	P	P

[a] The values in parentheses are CCG (mM). Inverted tube test code G: transparent gel, OG: opaque gel, I: Insoluble, S: soluble, P: soluble after heating but precipitate upon cooling to room temperature.

Table S3. Gelation properties and critical concentration for gelation (CCG) of brominated compounds **5**.[a]

Solvent	5a	5b	5c	5d	5e	5f
Ethyl ether	P	G (21.8)	G (6.34)	G (5.20)	G (4.49)	G (6.95)
Dichloromethane	S	P	G (15.6)	G (9.10)	G (2.69)	G (5.01)
Acetone	P	P	G (6.34)	OG (9.71)	G (3.74)	G (6.26)
Chloroform	S	S	S	G (16.2)	G (11.2)	G (8.94)
Methanol	P	P	P	P	P	P
THF	S	S	S	G (72.8)	G (13.5)	G (15.6)
Isopropyl ether	P	P	G (2.27)	G (4.85)	G (13.5)	G (8.35)
n-Hexane	P	P	P	P	P	OG (41.7)
Ethyl acetate	P	G (43.5)	G (3.30)	G (4.85)	G (4.49)	G (8.35)
CCl_4	P	G (87.0)	OG (52.9)	OG (29.1)	G (16.8)	G (17.9)
Ethanol	S	G (14.5)	G (3.17)	G (4.41)	G (4.49)	G (6.26)
Methyl ethylketone	S	P	G (7.93)	OG (11.2)	G (6.73)	G (8.35)
Cyclohexane	P	P	OG (8.81)	G (8.09)	OG (33.7)	G (8.94)
Acetonitrile	P	G (3.48)	G (0.32)	G (0.29)	G (0.67)	G (1.51)
Isopropanol	S	G (43.5)	G (19.8)	G (3.64)	G (13.5)	G (11.4)
1,2-Dichloroethane	S	P	G (3.60)	G (7.28)	G (2.99)	G (13.9)
Triethylamine	P	OG (43.5)	G (7.93)	G (7.28)	G (4.85)	G (8.94)
1-Propanol	S	G (17.4)	OG (7.93)	G (8.09)	G (11.2)	G (8.94)
n-Heptane	P	P	OG (22.7)	OG (9.71)	G (22.4)	G (8.35)
Water	I	I	I	I	I	I
Dioxane	S	P	OG (15.9)	G (6.62)	G (6.73)	OG (7.82)
Toluene	P	P	G (22.7)	G (12.1)	G (33.7)	G (10.4)
Methylisobutylketone	-	G (29.0)	G (39.6)	OG (72.8)	OG (22.4)	OG (31.2)
Acetic acid	-	P	P	P	P	P
1-Butanol	S	G (29.0)	G (19.8)	G (18.2)	G (13.5)	OG (15.6)
1-Pentanol	-	G (29.0)	OG (10.6)	G (10.4)	G (13.5)	OG (20.9)
Benzyl alcohol	-	G (29.0)	G (19.8)	G (72.8)	G (16.8)	G (10.4)
Xylene	P	P	G (8.81)	G (9.71)	G (22.4)	G (15.6)
DMF	-	P	P	P	OG (4.85)	OG (4.17)
Cyclohexanol	-	G (87.0)	G (26.4)	OG (72.8)	OG (33.7)	OG (31.2)
TEOS	P	P	OG (14.4)	OG (8.83)	G (3.37)	G (6.26)
n-Decane	P	P	P	P	OG (11.2)	OG (20.9)
DMSO	-	OG (14.5)	OG (13.2)	OG (4.85)	OG (4.49)	OG (4.81)
1-Octanol	P	P	G (39.6)	G (14.6)	OG (33.7)	OG (20.9)

[a] The values in parentheses are CCG (mM). Inverted tube test code G: transparent gel, OG: opaque gel, I: Insoluble, S: soluble, P: soluble after heating but precipitate upon cooling to room temperature.

Table S4. Gelation properties and critical concentration for gelation (CCG) of iodinated compounds **6**.[a]

Solvent	6b	6c	6d	6e	6f
Ethyl ether	P	I	P	P	P
Dichloromethane	P	G (13.8)	G (4.91)	G (14.9)	P
Acetone	P	G (7.67)	G (8.01)	P	G (2.81)
Chloroform	S	G (69.0)	G (12.8)	P	P
Methanol	P	P	P	P	OG (9.34)
THF	S	S	G (32.0)	P	P
Isopropyl ether	P	OG (23.0)	P	P	P
***n*-Hexane**	P	OG (6.27)	G (4.91)	OG (19.9)	P
Ethyl acetate	P	OG (13.8)	G (5.43)	P	P
CCl_4	P	P	P	P	P
Ethanol	P	G (5.75)	OG (8.01)	P	OG (6.23)
Methyl ethylketone	P	G (23.0)	G (10.7)	P	OG (18.7)
Cyclohexane	P	OG (13.8)	OG (10.7)	P	P
Acetonitrile	P	P	P	P	P
Isopropanol	P	P	OG (16.0)	P	P
1,2-Dichloroethane	P	G (13.8)	OG (9.15)	P	P
dimethoxyethane	S	G (13.8)	G (12.8)	P	P
Triethylamine	P	G (11.5)	G (4.91)	G (59.6)	P
1-propanol	P	G (11.5)	G (21.3)	P	P
***n*-heptane**	P	OG (4.60)	G (21.3)	P	
Water	I	I	I	I	I
Dioxane	P	P	G (5.34)	P	
Toluene	P	P	P	P	P
Methylisobutylketone	P	P	G (12.8)	P	
Acetic acid	P	P	P	P	P
1-Butanol	P	G (17.3)	G (32.0)	P	P
1-Pentanol	P	G (11.0)	G (5.82)	P	
2-propylbenzene		OG (69.0)	G (16.0)		
Cyclohexanol		G (69.0)	P	P	
2-Methoxyethylether		G (69.0)	G (32.0)		
TEOS		P	P	P	P
***n*-Decane**		OG (13.8)	OG (21.3)	P	
DMSO		OG (8.63)	P	OG (19.9)	OG (4.31)
1-Octanol		G (23.0)	OG (32.0)		

[a] The values in parentheses are CCG (mM). Inverted tube test code G: transparent gel, OG: opaque gel, I: Insoluble, S: soluble, P: soluble after heating but precipitate upon cooling to room temperature.

Table S5. Comparative gelation ability and critical concentration for gelation (CCG) of halogenated compounds with Cl (**4d**), Br (**5d**) and I (**6d**) bearing the same alkyl chain length.[a]

Solvent	4e	5e	6e
***n*-Hexane**	P	P	OG (19.9)
***n*-Heptane**	P	G (22.4)	P
***n*-Decane**		OG (11.2)	P
Cyclohexane	P	OG (33.7)	P
Ethyl ether	P	G (4.49)	P
Isopropyl ether	OG (76.5)	G (13.5)	P
1,2-Dichloroethane	P	G (2.99)	P
Dichloromethane	P	G (2.69)	G (14.9)
CCl_4	P	G (16.8)	P
Chloroform	S	G (11.2)	P
Acetonitrile	P	G (0.673)	P
Ethyl acetate	OG (76.5)	G (4.49)	P
Ethanol	OG (76.5)	G (4.49)	P
Isopropanol	P	G (13.5)	P
1-Propanol	P	G (11.2)	P
1-Butanol		G (13.5)	
1-Pentanol		G (13.5)	P
Cyclohexanol			
1-Octanol		OG (33.7)	
1-Dodecanol			
Acetone	P	G (3.74)	P
Methylethylketone	OG (76.5)	G (6.73)	P
Dimethoxyethane			P
Triethylamine		G (4.85)	
DMSO		OG (4.49)	
Dioxane		G (6.73)	
Toluene		G (33.7)	
Pyridine		G (16.8)	
TEOS		G (3.37)	

[a] The values in parentheses are CCG (mM). Inverted tube test code G: transparent gel, OG: opaque gel, S: Soluble, I: Insoluble, S: soluble, P: soluble after heating but precipitate upon cooling.

Table S6. Comparative gelation ability and critical concentration for gelation (CCG) of halogenated compounds with Cl (**4d**), Br (**5d**) and I (**6d**) bearing the same alkyl chain length.[a]

Solvent	3f	4f	5f	6f
***n*-Hexane**	OG (18.5)	P	OG (41.7)	P
***n*-Heptane**		OG (70.4)	G (8.35)	
***n*-Decane**			OG (20.9)	
Cyclohexane	P	OG (70.4)	G (8.94)	P
Ethyl ether	P	P	G (6.95)	P
Isopropyl ether	P	P	G (8.35)	P
1,2-Dichloroethane	OG (36.9)	OG (70.4)	G (13.9)	P
Dichloromethane	P	P	G (5.01)	P
CCl_4	P	P	G (17.9)	P
Chloroform	P	P	G (8.94)	P
Acetonitrile	P	I	G (1.51)	P
Ethyl acetate	P	P	G (8.35)	P
Ethanol	P	P	G (6.26)	OG (6.23)
Isopropanol	P	OG (23.5)	G (11.4)	P
1-Propanol	P	OG (23.5)	G (8.94)	P
1-Butanol			OG (15.6)	P
1-Pentanol			OG (20.9)	
Cyclohexanol			OG(31.2)	
1-Octanol	OG (73.8)		OG (20.9)	
1-Dodecanol				
Acetone	P	G (35.2)	G (6.26)	G (2.81)
Methylethylketone	P	OG (70.4)	G (8.35)	OG (18.7)
Dimethoxyethane				P
Triethylamine			G (8.94)	P
DMSO	OG (73.8)		OG (4.81)	OG (4.31)
Dioxane			OG (7.82)	
Toluene			G (10.4)	P
Pyridine			G (15.6)	
TEOS			G (6.26)	P

[a] The values in parentheses are CCG (mM). Inverted tube test code G: transparent gel, OG: opaque gel, S: Soluble, I: Insoluble, S: soluble, P: soluble after heating but precipitate upon cooling.

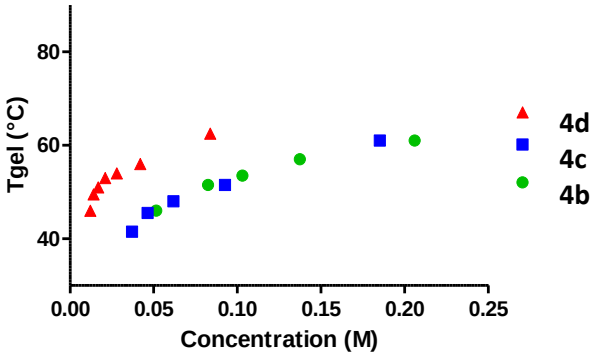


Fig. S1. T_{gel} vs. concentration plot for the chlorinated gelators in ethanol

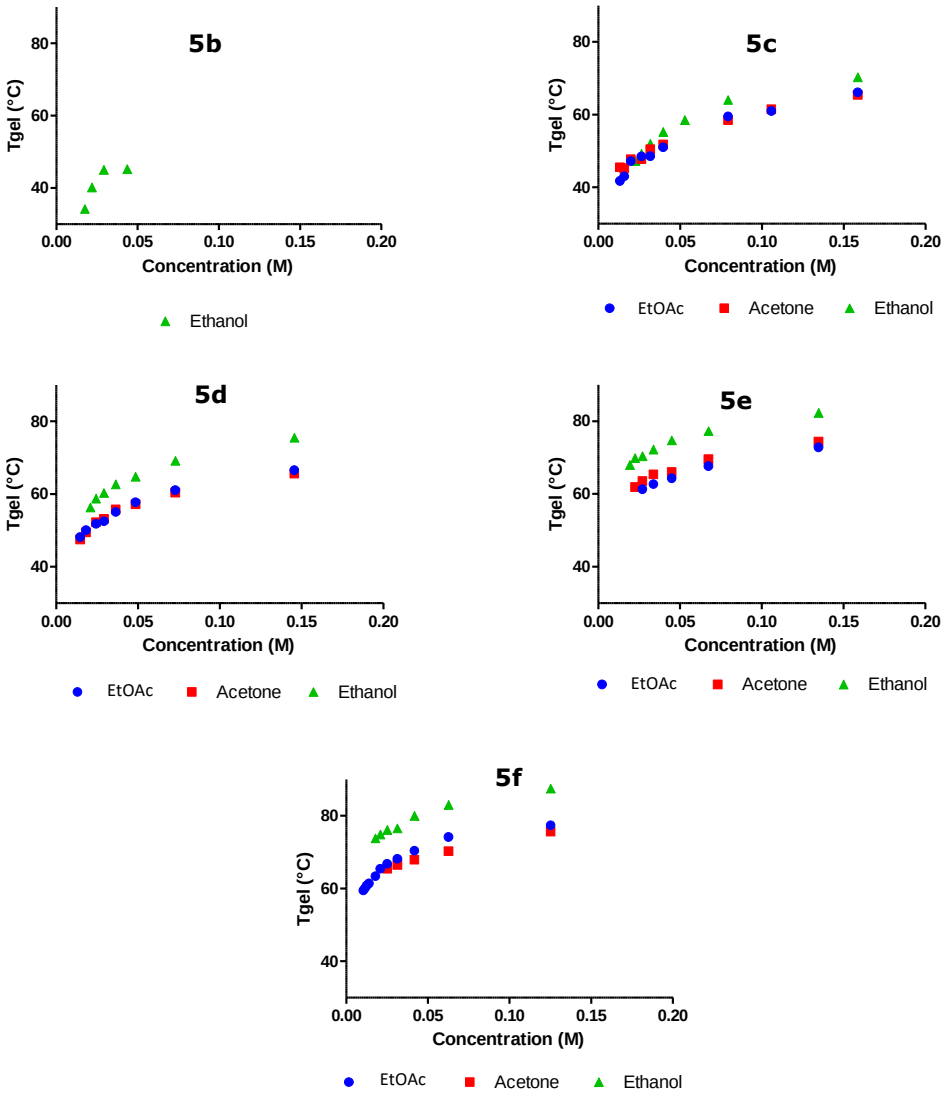


Fig. S2. T_{gel} vs. concentration plot for the brominated gelators **5b-f** in ethyl acetate (EtOAc), acetone and ethanol.

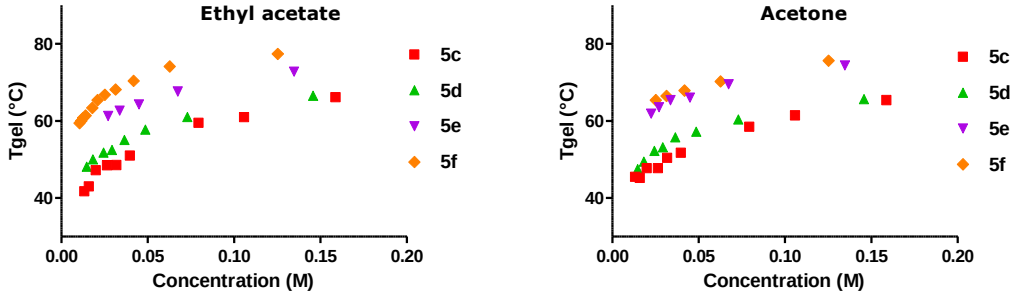


Fig. S3. T_{gel} vs concentration plot for brominated gelators **5** in ethyl acetate and Acetone

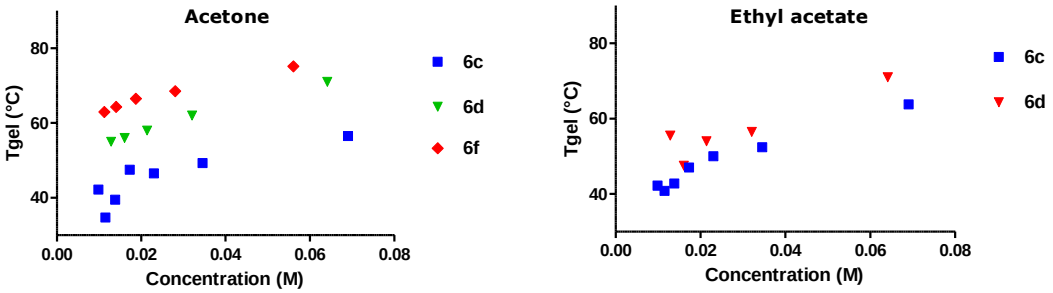


Fig S4. T_{gel} vs concentration plot for Iodinated gelators **6c-f**

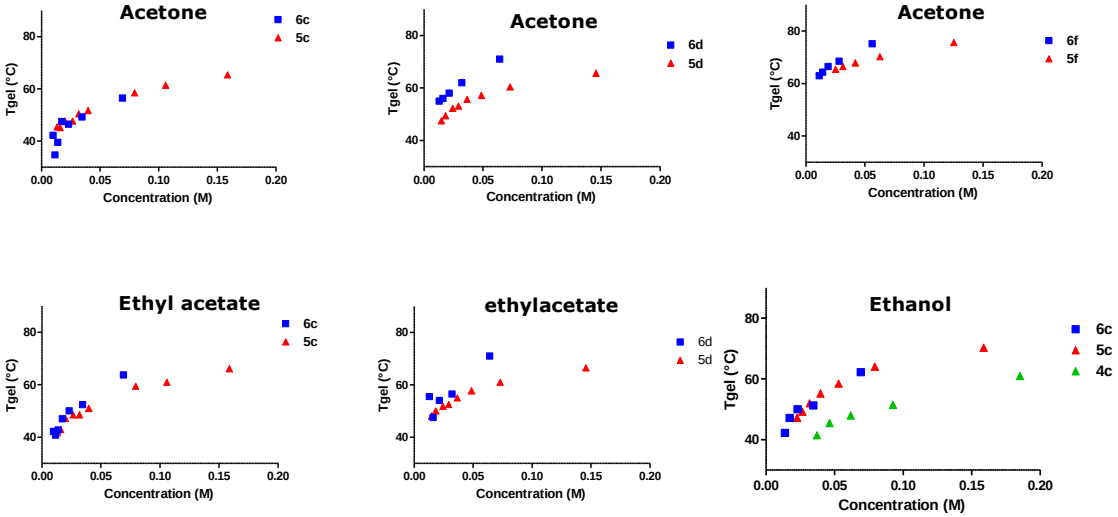


Fig. S5. T_{gel} vs concentration plots for chlorinated (**4c**), brominated (**5c,d,f**) and Iodinated (**6c,d,f**) gelators.

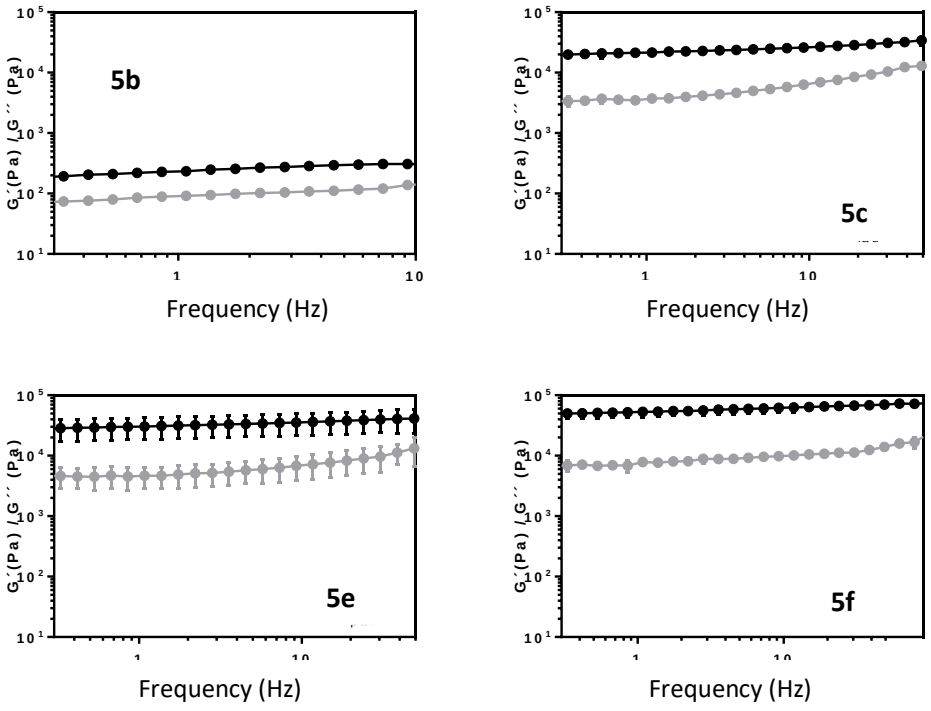


Fig. S6 Alkyl chain length effect on the rheological properties of gels in ethanol of brominated analogues: **5b**, **5c**, **5e** and **5f**. G´modulus (black circles) and G" modulus (grey circles) T: 25°C, deformation: 0,1%.

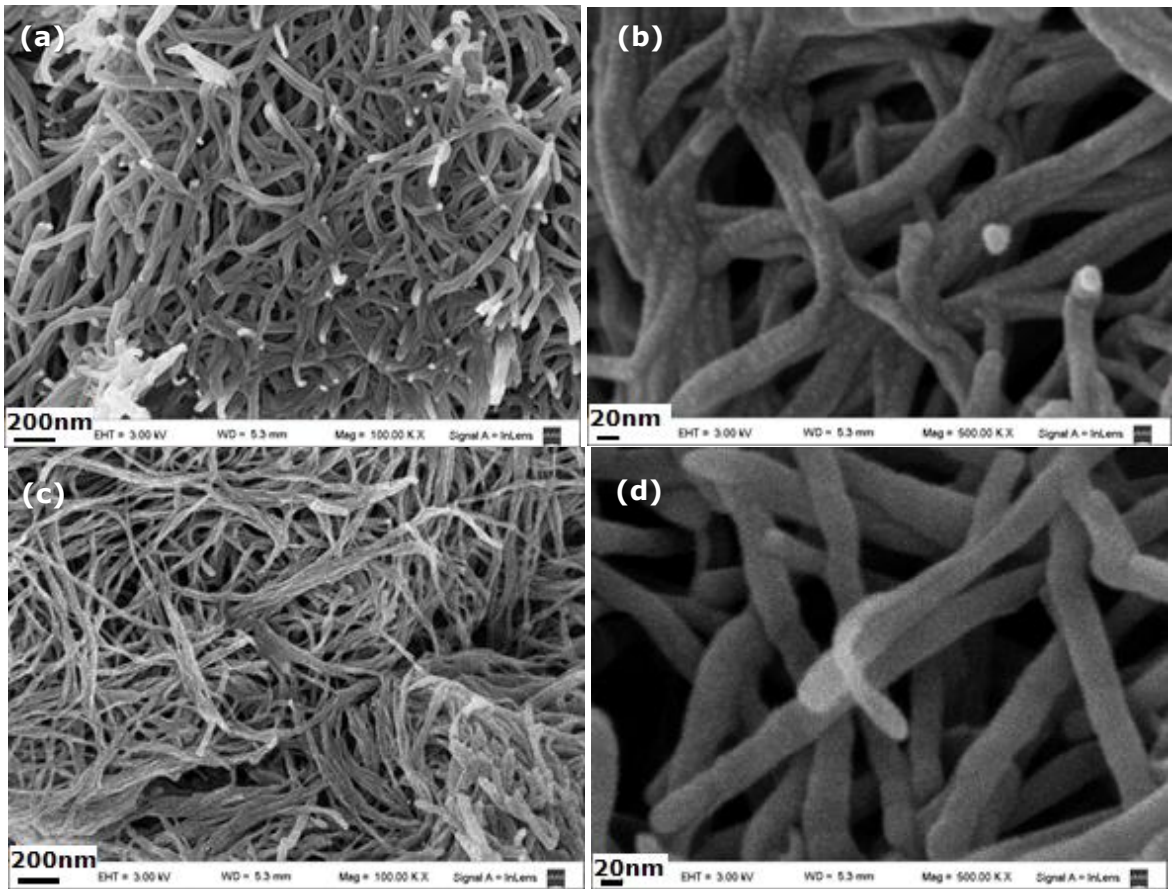


Fig. S7 SEM images of the aerogels obtained from gels of the chlorinated gelators: (a,b) **4c** in ethanol and (c,d) **4f** in ethanol.

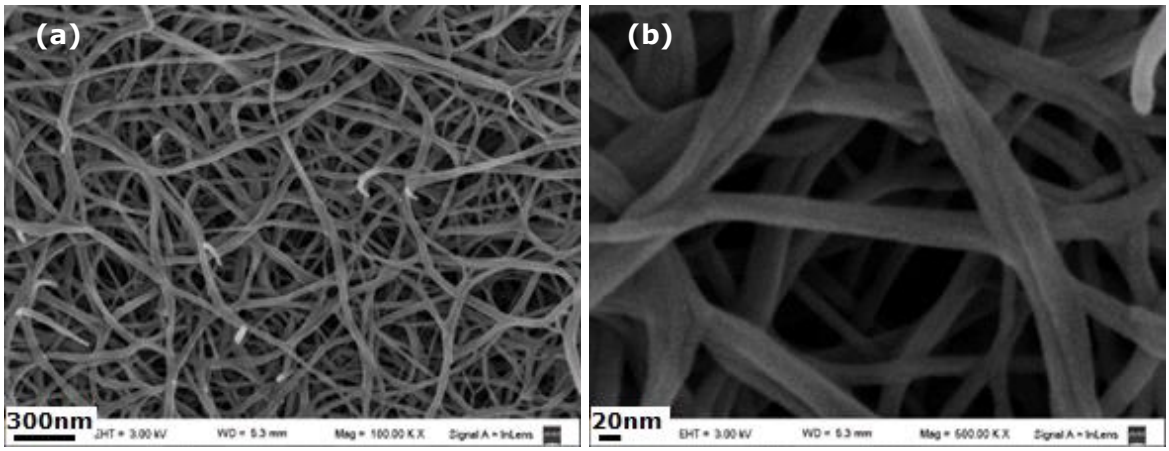


Fig. S8 SEM images of the aerogels obtained from gels in acetonitrile of gelator **5c**.

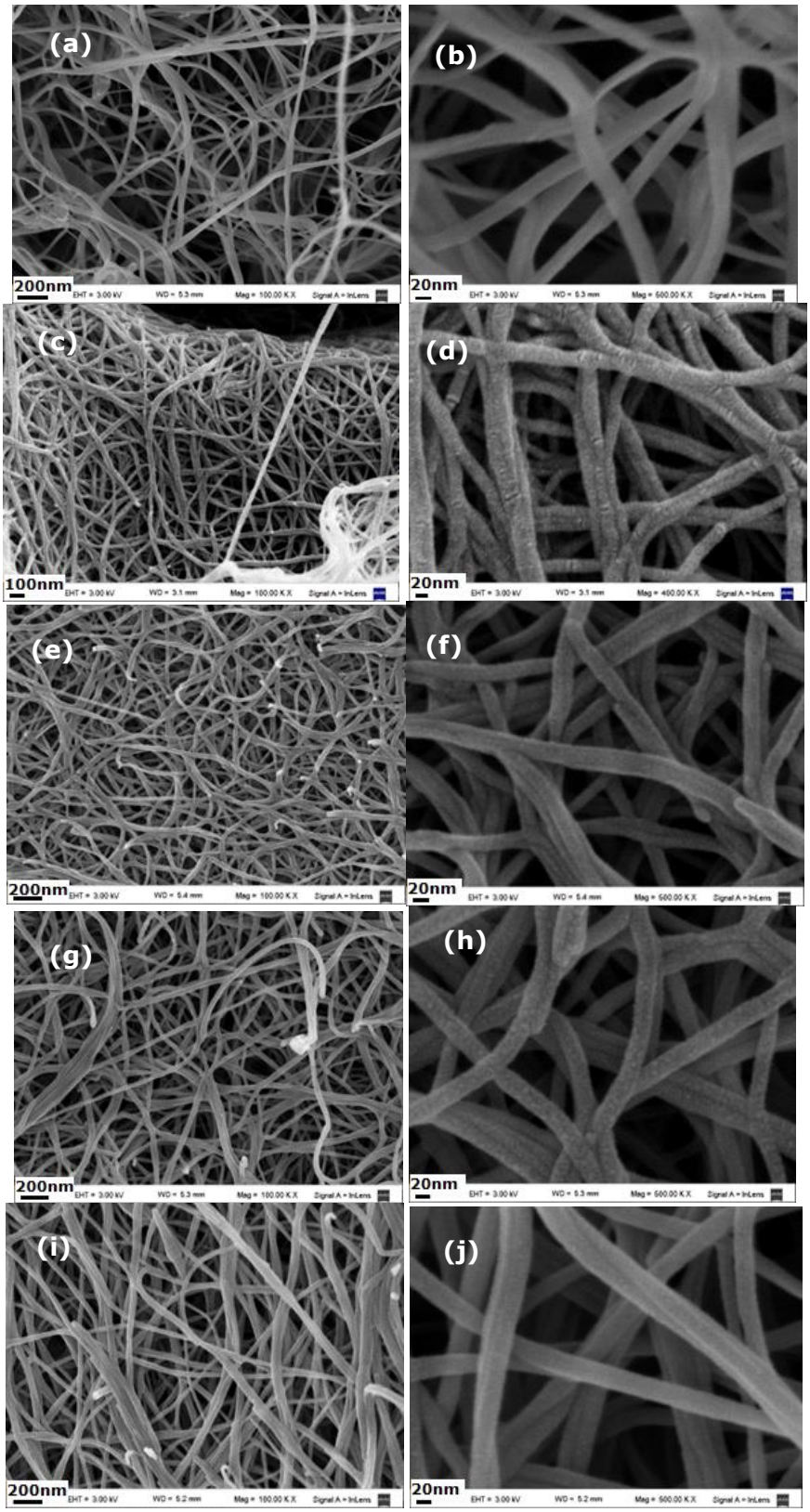


Fig. S9 SEM images of aerogels obtained from brominated gelators from gels in ethanol of: (a,b) **5b**; (c,d) **5c**; (e,f) **5d**; (g,h) **5e** and (i,j) **5f**.

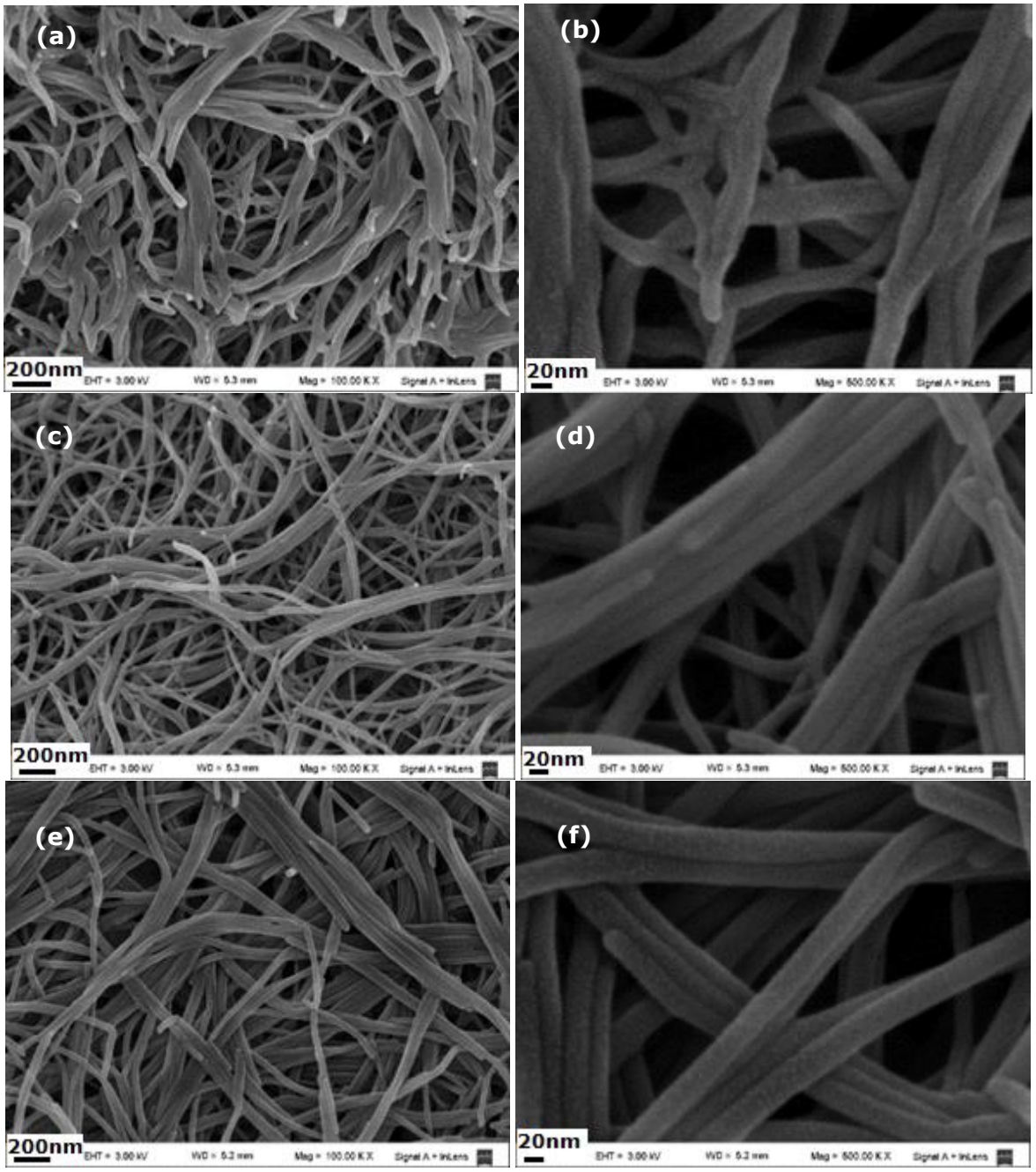


Fig. S10 SEM images of aerogels obtained from gels in ethanol of iodinated gelators: **6c** (a,b); **6d** (c,d) and **6f** (e,f).

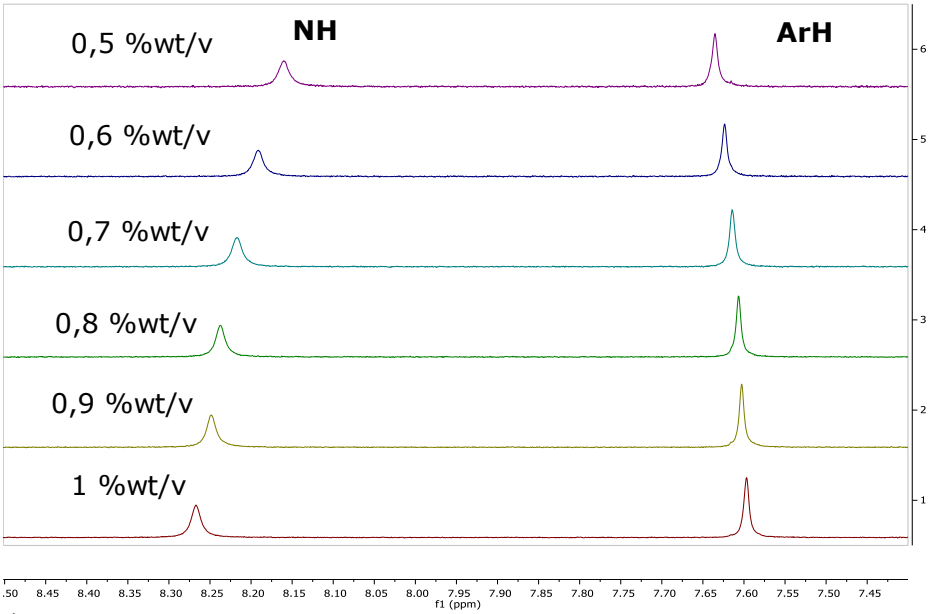


Fig. S11. ^{1}H NMR spectra vs gelator concentration (**5f**) in $CDCl_3$. For clarity only the zone with the N-H and Ar-H signals are shown. CCG 0.71 %wt/v. the experiment started with the higher concentration, subsequent dilutions were performed followed by a heating cooling process and a stabilization period of 15 minutes.

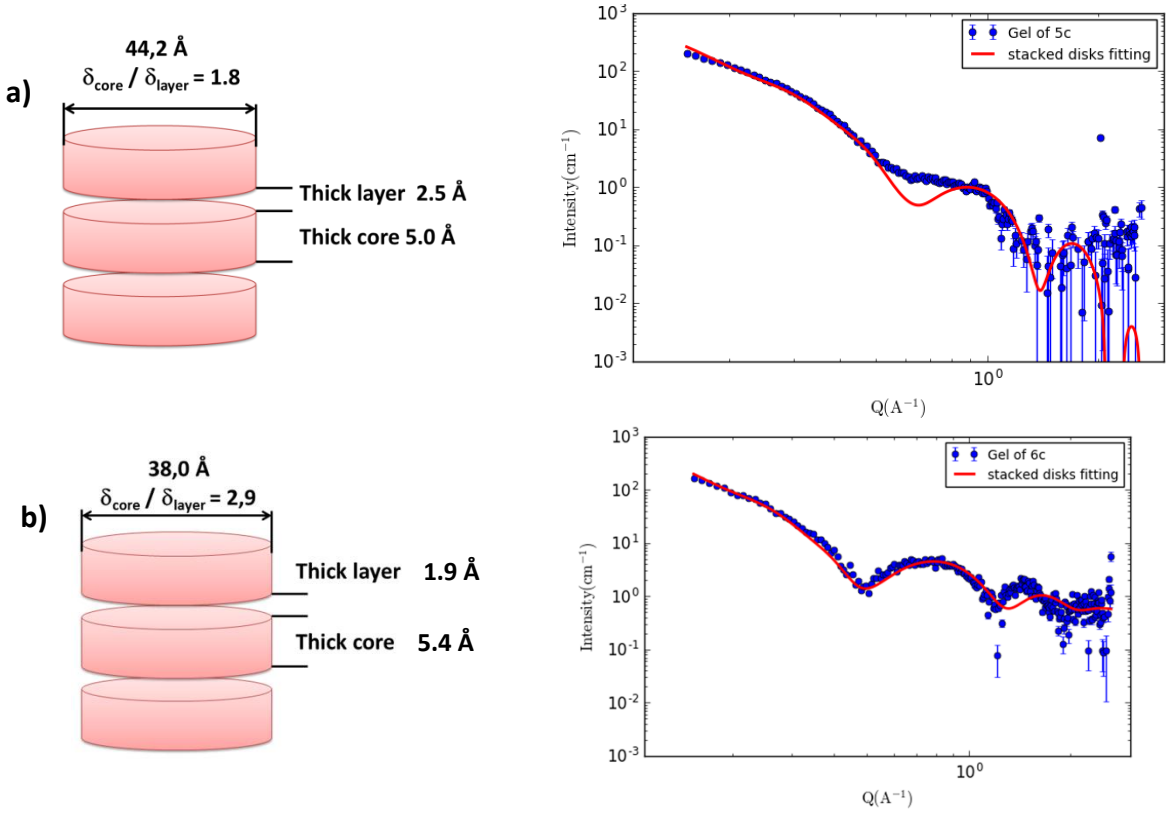


Fig. S12 SAXS and stacked discs cylinder fitting obtained for the brominated gel **5c** in ethanol (a) and Iodinated gel of **6c** in 1-pentanol (b).

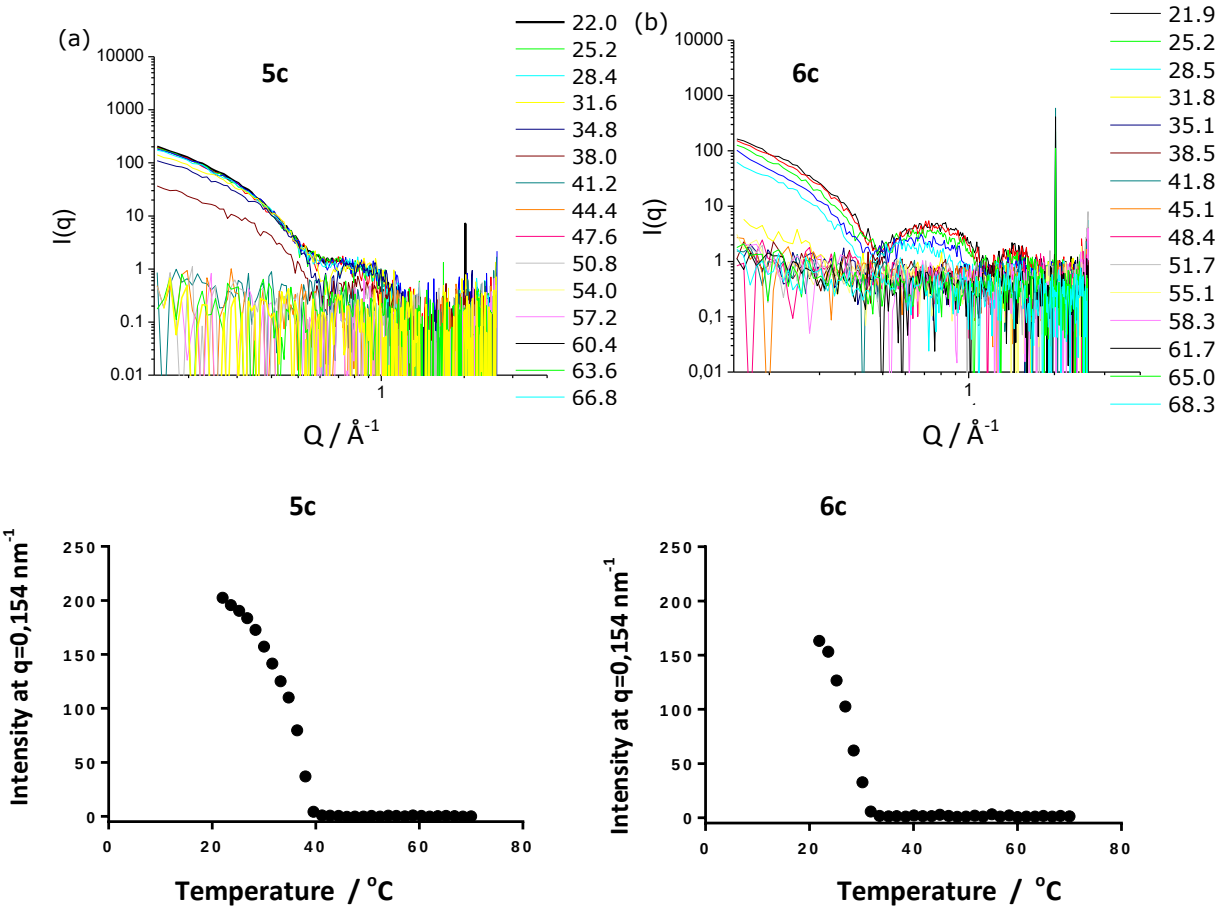


Fig S13. Temperature dependent SAXS measurements (20-70 °C) for gels of **5c** in etanol and **6c** in pentanol. As the temperature raised the structure factor decreased and abruptly disappeared after the T_{gel} was reached, as can be observed in the Intensity vs temperature plots at q=0,154 $Å^{-1}$

Table S7 Crystal data and structure refinement for **7.**

	Compound 7
Empirical formula	$C_{18}H_{27}Cl_2NO$
Formula weight	344.30
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.382(2)
b/Å	12.2314(14)
c/Å	9.8293(7)
α/°	90
β/°	102.916(9)
γ/°	90
Volume/Å^3	1919.8(4)
Z	4
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	0.340
F(000)	736.0
Crystal size/mm^3	0.3 × 0.25 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.656 to 57.878
Index ranges	-21 ≤ h ≤ 21, -15 ≤ k ≤ 13, -12 ≤ l ≤ 13
Reflections collected	12878
Independent reflections	4456 [R_{int} = 0.0482, R_{sigma} = 0.0594]
Data/restraints/parameters	4456/0/200
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1136
Final R indexes [all data]	R_1 = 0.1241, wR_2 = 0.1445
Largest diff. peak/hole / e Å^{-3}	0.29/-0.25

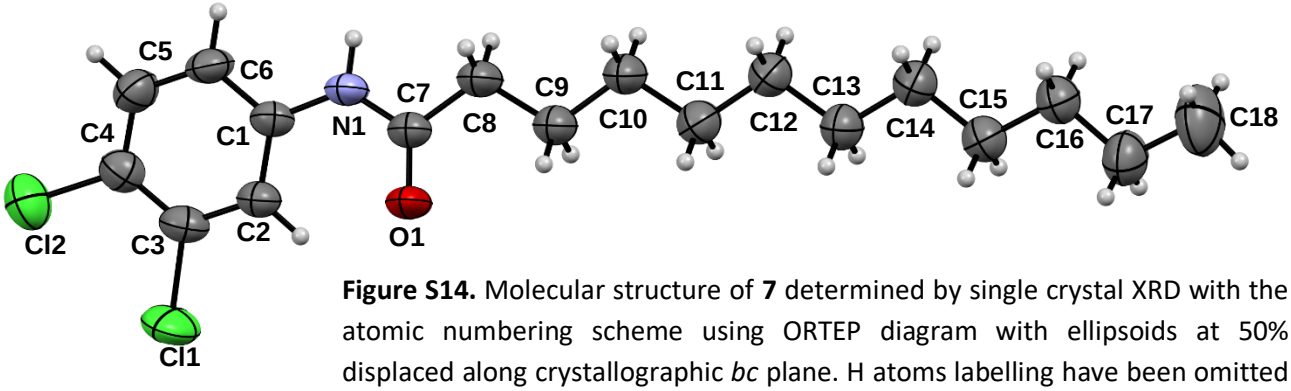


Figure S14. Molecular structure of **7** determined by single crystal XRD with the atomic numbering scheme using ORTEP diagram with ellipsoids at 50% displaced along crystallographic *bc* plane. H atoms labelling have been omitted for clarity. Colour code: H, light grey; C, grey; N, light blue; O, red; Cl, green.

Table S8 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **7**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl2	4615.5(5)	-2469.0(6)	11144.0(8)	86.5(3)
Cl1	4708.9(6)	-521.2(7)	13293.4(6)	101.3(3)
N1	3273.1(12)	1884.0(16)	9185.6(16)	55.0(5)
C1	3597.1(14)	865(2)	9701(2)	48.4(6)
C7	3056.4(15)	2740(2)	9892(2)	52.7(6)
C3	4260.0(15)	-337(2)	11533(2)	58.2(7)
O1	3122.6(12)	2728.9(14)	11157.7(14)	68.4(5)
C2	3953.0(15)	685(2)	11100(2)	55.2(6)
C14	1266.3(18)	9636(2)	9079(2)	69.2(7)
C6	3580.8(16)	13(2)	8774(2)	61.9(7)
C12	1748.3(19)	7660(2)	8928(3)	68.3(7)
C15	1206.9(18)	10581(2)	10047(2)	68.2(7)
C10	2242.2(18)	5683(2)	8916(2)	68.3(7)
C13	1681.4(17)	8642(2)	9838(2)	67.1(7)
C11	2163.5(18)	6690(2)	9758(2)	67.0(7)
C4	4233.2(15)	-1185(2)	10608(2)	58.4(6)
C9	2632.3(17)	4728(2)	9807(2)	62.6(7)
C5	3892.8(17)	-994(2)	9212(2)	67.5(7)
C8	2700.8(18)	3703(2)	9000(2)	68.0(8)
C16	782.3(18)	11591(2)	9364(3)	71.6(8)
C17	729(2)	12504(2)	10381(3)	82.9(9)
C18	307(2)	13525(3)	9725(4)	115.6(12)

Table S9 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **7.** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl2	96.7(6)	67.6(5)	92.3(5)	13.1(4)	15.4(4)	19.9(4)
Cl1	137.5(7)	105.6(7)	46.9(4)	14.5(4)	-9.1(4)	35.2(6)
N1	76.2(14)	59.1(13)	30.0(8)	2.4(9)	12.2(9)	8.5(11)
C1	51.7(14)	57.4(15)	37.0(11)	1.2(11)	11.5(10)	0.7(12)
C7	64.6(16)	56.6(16)	36.5(11)	0.5(11)	10.7(11)	1.5(13)
C3	58.0(16)	73.7(18)	40.6(11)	6.8(12)	5.7(11)	4.3(14)
O1	108.5(15)	64.8(11)	31.7(8)	1.9(7)	15.4(8)	15.1(10)
C2	66.1(16)	60.0(16)	37.2(11)	1.6(11)	7.0(10)	3.5(13)
C14	82.9(19)	58.2(17)	62.9(15)	-3.3(13)	8.7(13)	3.5(15)
C6	75.7(17)	71.9(19)	35.5(11)	-7.4(12)	6.8(11)	8.4(15)
C12	85(2)	58.0(17)	57.9(14)	-4.5(13)	7.2(13)	7.3(15)
C15	80.3(19)	60.2(17)	61.7(15)	0.7(13)	10.5(13)	5.2(15)

C10	96(2)	58.1(17)	46.9(13)	-0.8(12)	6.9(13)	12.2(16)
C13	81.4(19)	56.7(17)	61.2(15)	-1.7(13)	11.5(13)	9.7(15)
C11	80.0(19)	60.6(17)	56.8(14)	-3.8(13)	7.5(13)	7.5(15)
C4	58.0(15)	61.8(17)	55.7(14)	6.6(13)	13.2(11)	5.5(13)
C9	81.2(18)	59.9(17)	44.7(12)	0.4(12)	9.7(12)	8.7(15)
C5	82.6(19)	63.5(18)	55.3(14)	-9.6(13)	12.9(13)	12.8(16)
C8	101(2)	64.2(18)	38.0(11)	2.2(12)	12.9(12)	13.0(16)
C16	82.1(19)	59.4(18)	70.1(16)	2.6(14)	10.3(14)	8.7(16)
C17	94(2)	61.7(19)	91(2)	-3.2(16)	16.0(17)	10.0(17)
C18	115(3)	73(2)	152(3)	8(2)	16(2)	27(2)

Table S10 Bond Lengths for **7.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl2	C4	1.728(3)	C14	C13	1.507(3)
Cl1	C3	1.737(2)	C6	C5	1.365(3)
N1	C1	1.404(3)	C12	C13	1.517(3)
N1	C7	1.348(3)	C12	C11	1.512(3)
C1	C2	1.386(3)	C15	C16	1.501(3)
C1	C6	1.380(3)	C10	C11	1.506(3)
C7	O1	1.224(2)	C10	C9	1.513(3)
C7	C8	1.505(3)	C4	C5	1.381(3)
C3	C2	1.379(3)	C9	C8	1.502(3)
C3	C4	1.374(3)	C16	C17	1.514(4)
C14	C15	1.514(3)	C17	C18	1.501(4)

Table S11 Bond Angles for **7.**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C7	N1	C1	128.75(17)	C11	C12	C13	112.7(2)
C2	C1	N1	122.7(2)	C16	C15	C14	115.8(2)
C6	C1	N1	118.82(19)	C11	C10	C9	112.99(19)
C6	C1	C2	118.5(2)	C14	C13	C12	115.5(2)
N1	C7	C8	114.81(17)	C10	C11	C12	115.4(2)
O1	C7	N1	122.8(2)	C3	C4	Cl2	121.95(18)
O1	C7	C8	122.4(2)	C3	C4	C5	118.4(2)
C2	C3	Cl1	117.95(19)	C5	C4	Cl2	119.7(2)
C4	C3	Cl1	120.3(2)	C8	C9	C10	114.25(18)
C4	C3	C2	121.7(2)	C6	C5	C4	120.4(2)
C3	C2	C1	119.5(2)	C9	C8	C7	114.21(18)
C13	C14	C15	112.9(2)	C15	C16	C17	113.6(2)
C5	C6	C1	121.5(2)	C18	C17	C16	114.8(3)

Table S12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **7.**

Atom	*x*	*y*	*z*	U(eq)
H1	3204	1974	8299	66
H2	3984	1250	11743	66
H14A	707	9440	8571	83
H14B	1581	9868	8403	83
H6	3352	127	7831	74
H12A	1191	7450	8425	82
H12B	2067	7862	8246	82
H15A	908	10333	10737	82
H15B	1769	10776	10540	82
H10A	2581	5854	8252	82
H10B	1690	5472	8392	82
H13A	1371	8427	10527	81
H13B	2241	8844	10337	81
H11A	2719	6908	10257	80
H11B	1846	6503	10448	80
H9A	3188	4938	10315	75
H9B	2301	4573	10487	75
H5	3876	-1554	8566	81
H8A	3052	3849	8347	82
H8B	2148	3510	8461	82
H16A	220	11402	8863	86
H16B	1085	11853	8686	86
H17A	428	12237	11059	100
H17B	1292	12689	10881	100
H18A	603	13803	9059	173
H18B	308	14064	10435	173
H18C	-260	13360	9262	173

Table S13 Hydrogen Bonds for **7.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O1^1	0.86	2.11	2.969(2)	175.4

Table S14. Crystal Data and Refinement Details for Structures for **5a**

	Compound 5a
Empirical formula	$C_{20}H_{30}Br_2N_2O_2$
Formula weight	490.28
Temperature/K	170(1)
Crystal system	monoclinic
Space group	C2/c
a/Å	14.5709(14)
b/Å	17.1752(12)
c/Å	8.9783(10)
α/°	90
β/°	103.868(11)
γ/°	90
Volume/Å^3	2181.4(4)
Z	4
ρ_{calc}g/cm^3	1.493
μ/mm^{-1}	3.732
F(000)	1000.0
Crystal size/mm^3	0.20 × 0.10 × 0.10
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.464 to 58.62
Index ranges	-20 ≤ h ≤ 19, -22 ≤ k ≤ 22, -11 ≤ l ≤ 11
Reflections collected	7402
Independent reflections	2551 [R_{int} = 0.0641, R_{sigma} = 0.0834]
Data/restraints/parameters	2551/0/119
Goodness-of-fit on F^2	0.998
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.0706
Final R indexes [all data]	R_1 = 0.0879, wR_2 = 0.0845
Largest diff. peak/hole / e Å^{-3}	0.51/-0.38

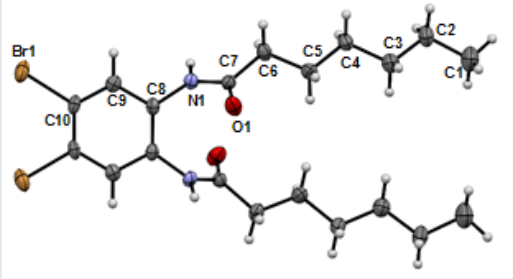


Figure S15. Molecular structure of **5a** determined by single crystal XRD with the atomic numbering scheme using ORTEP diagram with ellipsoids at 50%. Labelling is shown for the asymmetric unit; H atoms labelling have been omitted for clarity. Colour code: H, light grey; C, grey; N, light blue; O, red; Br, bronze.

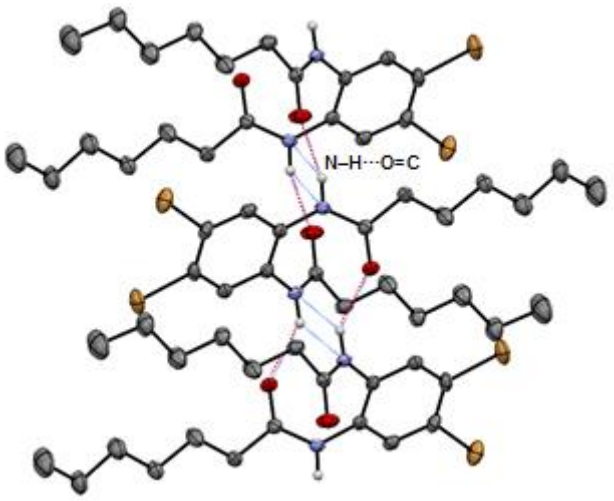


Figure 16. N–H···O=C H-bond motifs (red) and N–H interactions (blue) in **5a**.

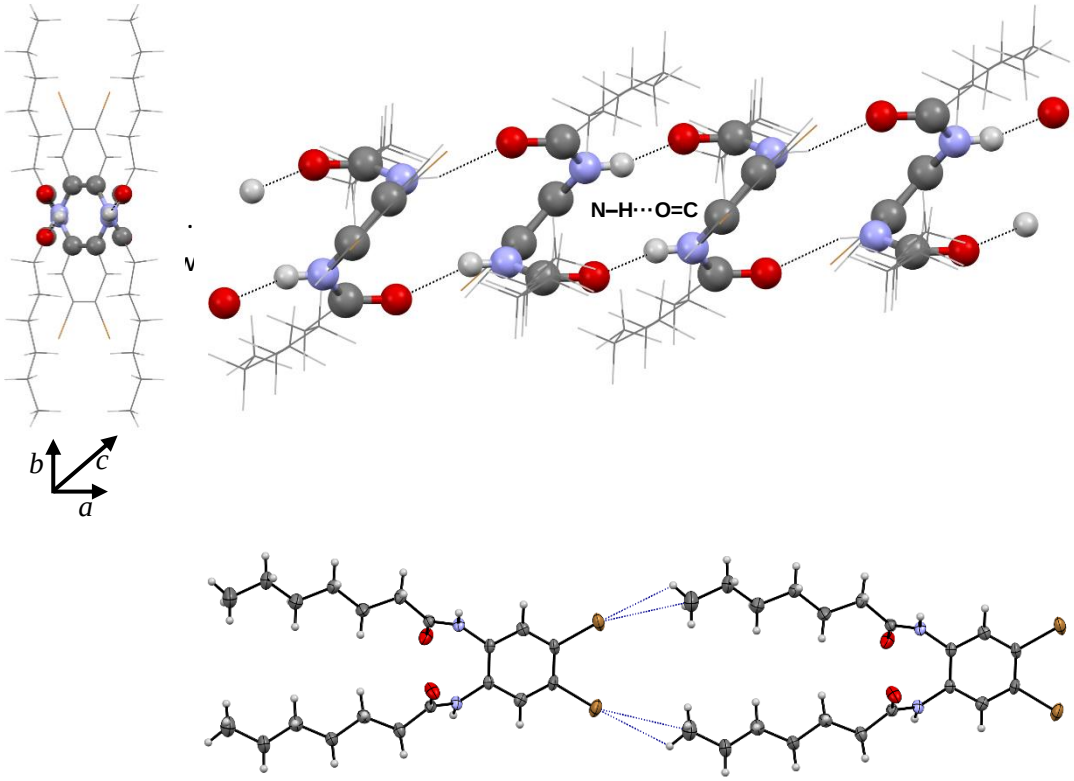


Figure S17. Interaction developed between Br substituents and methyl groups.

Table S15 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **5a.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	4221.9(3)	13095.5(2)	3624.4(5)	39.36(15)
N1	4246.6(18)	10073.7(15)	3384(3)	23.0(7)
C6	3477(2)	8822.9(19)	3283(4)	27.2(8)
C9	4337(2)	11461(2)	3356(3)	23.1(8)
C4	3310(2)	7363.1(19)	3534(4)	29.2(9)
C5	3642(3)	8031(2)	2689(5)	38.8(10)
C10	4668(2)	12159.4(19)	2947(4)	25.1(8)
C8	4649(2)	10755.3(19)	2911(3)	20.8(8)
C3	3529(3)	6569(2)	2977(5)	41.3(10)
C1	3604(3)	5116(2)	3477(6)	66.8(14)
O1	3814.2(18)	9456.7(14)	1098(2)	35.4(7)
C7	3860(2)	9472.8(19)	2482(4)	23.3(8)
C2	3283(3)	5903(2)	3915(5)	41.1(10)

Table S16 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5a.** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	41.4(3)	21.6(2)	52.5(3)	-8.3(2)	6.28(19)	5.40(19)
N1	34.9(17)	19.9(16)	15.8(15)	2.3(12)	9.3(13)	0.7(14)
C6	36(2)	23(2)	22.6(19)	0.1(16)	7.7(16)	-5.0(17)
C9	26.5(19)	24(2)	17.1(18)	-0.2(15)	1.6(15)	2.8(16)
C4	30(2)	23(2)	36(2)	3.1(17)	10.7(17)	-1.4(17)
C5	49(3)	26(2)	51(2)	-0.1(19)	31(2)	-2(2)
C10	31(2)	14.7(19)	28(2)	-3.7(14)	2.0(16)	2.3(15)
C8	26(2)	17.3(19)	16.8(17)	0.8(14)	0.9(14)	0.2(15)
C3	47(3)	29(2)	54(3)	0(2)	23(2)	-2(2)
C1	81(4)	30(3)	100(4)	-5(3)	42(3)	-2(3)
O1	56.3(18)	32.0(15)	21.0(13)	-6.6(12)	15.6(12)	-14.1(13)
C7	28.6(19)	19.9(19)	22.8(19)	-0.2(15)	9.1(15)	1.4(16)
C2	48(3)	22(2)	54(3)	0.9(19)	15(2)	-3(2)

Table S17 Bond Lengths for **5a.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C10	1.889(3)	C4	C5	1.517(4)
N1	C8	1.420(4)	C4	C3	1.513(5)
N1	C7	1.349(4)	C10	C10[1]	1.396(7)
C6	C5	1.501(4)	C8	C8[1]	1.396(6)
C6	C7	1.506(4)	C3	C2	1.514(5)
C9	C10	1.376(4)	C1	C2	1.512(5)
C9	C8	1.386(4)	O1	C7	1.228(4)

[1]1-X,+Y,1/2-Z

Table S18 Bond Angles for **5a.**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C7	N1	C8	126.4(3)	C9	C8	N1	116.5(3)
C5	C6	C7	113.2(3)	C9	C8	$C8^1$	118.99(19)
C10	C9	C8	121.7(3)	$C8^1$	C8	N1	124.45(16)
C3	C4	C5	113.5(3)	C4	C3	C2	113.6(3)
C6	C5	C4	114.2(3)	N1	C7	C6	115.4(3)
C9	C10	Br1	119.1(2)	O1	C7	N1	122.6(3)
C9	C10	$C10^1$	119.28(19)	O1	C7	C6	122.0(3)
$C10^1$	C10	Br1	121.63(10)	C1	C2	C3	113.7(3)

^{1}1-X,+Y,1/2-Z

Table S19 Torsion Angles for **5a.**

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C4	C3	C2	C1	-173.3(3)	C8	N1	C7	O1	-0.2(5)
C5	C6	C7	N1	-142.4(3)	C8	C9	C10	Br1	-179.0(2)
C5	C6	C7	O1	38.2(5)	C8	C9	C10	$C10^1$	0.4(6)
C5	C4	C3	C2	174.5(3)	C3	C4	C5	C6	-176.9(3)
C10	C9	C8	N1	-179.2(3)	C7	N1	C8	C9	129.5(3)
C10	C9	C8	$C8^1$	3.0(5)	C7	N1	C8	$C8^1$	-52.9(6)
C8	N1	C7	C6	-179.6(3)	C7	C6	C5	C4	176.9(3)

^{1}1-X,+Y,1/2-Z

Table S20 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5a.**

Atom	*x*	*y*	*z*	U(eq)
H1	4249	10040	4363	28
H6A	3779	8847	4394	33
H6B	2789	8901	3154	33
H9	3882	11462	3958	28
H4A	3615	7408	4642	35
H4B	2619	7408	3412	35
H5A	4327	7967	2763	47
H5B	3311	8000	1591	47
H3A	4211	6543	3003	50
H3B	3174	6505	1897	50
H1A	4296	5098	3731	100
H1B	3360	5034	2372	100
H1C	3363	4708	4043	100
H2A	3577	6000	5013	49
H2B	2589	5891	3788	49

Table S21 Hydrogen Bonds for **5a.**

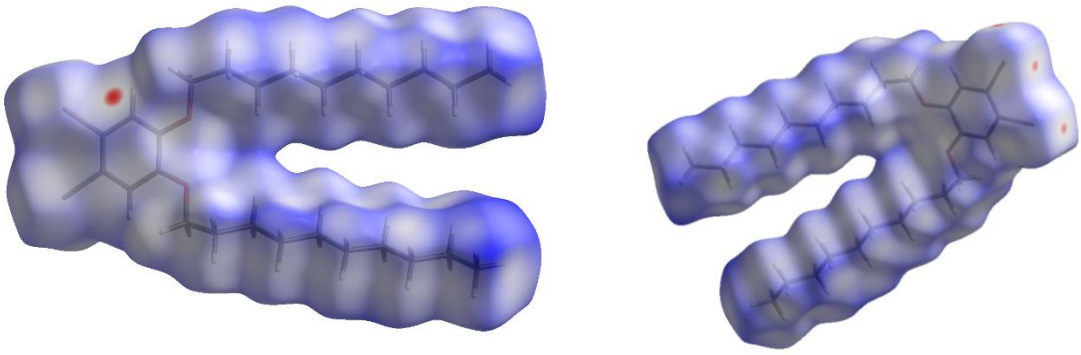
D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O1[1]	0.88	2.01	2.778(3)	144.9

[1]+X,2-Y,1/2+Z

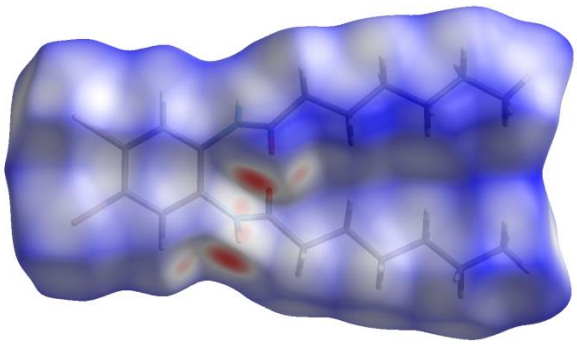
Hirshfeld surface analysis

Hirshfeld surfaces and fingerprint plots[5] were calculated using CrystalExplorer17 prpgram.[6] For the analysis, the X—H bond lengths (X = C, N) were converted to normalized values based on neutron diffraction results.[7]

Compound 1 Red zones (shorter contacts) located around the halogens and O atom



Compound 5a Red zones (shorter contacts) located around the amide moiety



Compound 7 Red zones (shorter contacts) located around the amide moiety.

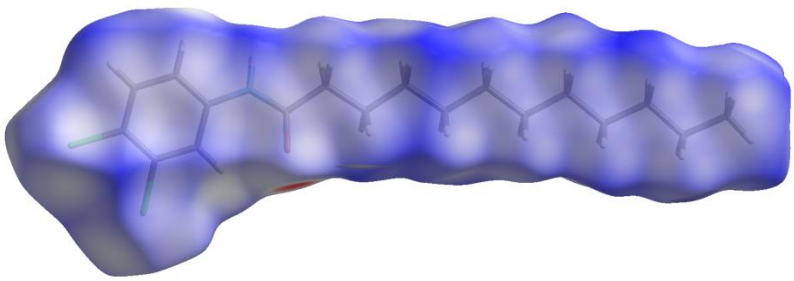


Table S22. Comparative analysis of results obtained from the decomposed fingerprint plots

Compound / Interaction (type, %)	1	5a	7
H···H	73.0	47.6	60.8
X···H	10.3	26.2	16.3
C···H	5.2	12.5	7.3
X···X	4.2	0.0	3.8
O···H	4.0	12.6	5.4
X···C	2.0	0.0	1.0
X···N	0.0	0.0	0.9
N…H	0.0	1.1	0.9
C···C	1.1	0.0	2.9
X···O	0.0	0.0	0.7
others	1.3	0.0	0.0

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