Title:	Star-shaped π-gelators based on oxadiazole and thiadiazoles: a structure–property correlation†
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Abstract:	Star-shaped and tetracatenar molecules based on 1,3,4-oxadiazole and thiadiazole derivatives were synthesized and their liquid crystallinity and gelation behavior were studied. The self-assembly and photophysical properties of these molecules are sensitive to the type of the heteroatom present in the molecule and the pattern of peripheral substitution. Only the star-shaped molecule with substituted oxadiazole arms exhibited a columnar hexagonal phase, while the tetracatenars were crystalline. This compound exhibited a supergelation behavior that is mainly supported by attractive π–π interactions. This is notable because usually supergelation is supported by H-bonding interactions. Further, this compound exhibited aggregation-induced emission with a several-fold increase in the luminescence intensity upon gelation. Surprisingly its thiadiazole counterpart was crystalline and did not gelate. The corresponding oxadiazole and thiadiazole star-shaped molecules, with peripheral 3,4-substitution, were liquid crystalline and stabilized gelation. This shows that in addition to π–π interactions, nanosegregation of incompatible molecular subunits like flexible tails plays a major role in organogelation and liquid crystalline self-assembly. Microscopy studies revealed a fibrillar network of several micrometers length confirming the long range molecular self-assembly. Electrochemical studies helped to understand the effect of peripheral substitution on the HOMO–LUMO levels and the band gaps.
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