Luminescent oligo(tetraphenyl)silole nanoparticles as chemical sensors for aqueous TNT

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Colloidal oligo(tetraphenyl)silole nanoparticles in THF/H_2O suspensions show increased luminescence and offer a method to detect TNT in an aqueous environment.

Aggregation-induced emission of silole species has recently been observed.[1,2] The large increase in luminescence from tetraphenylsilole aggregates has been attributed to the restricted rotation of the phenyl rings, which limits the nonradiative decay pathways;[3] however, the inhibition of solvent assisted quenching resulting from aggregation is another possible explanation.[4] Lifetime measurements show dramatically lengthened emission lifetimes in the solid state.[3,4] Siloles have also been shown to have potential as chemosensors for detecting oxidizing species, such as chromate[4,5] and explosives.[6,7] For example, poly(tetraphenyl)silole, **1**, has been shown to detect nitroaromatics, including TNT, with high sensitivity in organic solution.[7] Methods using capillary electrophoresis with sample preconcentration[8] have been developed to detect TNT well below the low to mid ppb concentration found in ground water near some military facilities.[9] Concentrations in ground water near unexploded ordinance have been measured as high as 500 ppb,[10] while concentrations in soil are often near 1000–5000 ppm.[11] The US Environmental Protection Agency has issued a Health Advisory Standard of 2 ppb for TNT.[12] Commercially available colorimetric kits are able to detect TNT above 500 ppb in soil, and in the 20–45 ppb range in water.[13] We report herein the sensing of TNT in aqueous media using nanoparticles of oligo(tetraphenyl)silole, produced by the precipitation of an organic solution of the oligomer with water. Photophysical properties of the nanoparticles are also discussed.

The luminescence properties of the nanoparticles depend greatly on the solution in which they are suspended. A colloid of **1** is prepared by rapid precipitation from a THF solution by the addition of water. A minimum volume-fraction of 60% water is needed to effect a sizable increase in luminescence, which indicates the onset of aggregation (Fig. 1). This critical water concentration is similar to that observed with other silole monomers, but less than the 80% needed to aggregate the more hydrophilic siloleamine.[4] The luminescence of colloids precipitated with 80 and 90% water are very similar, but the luminescence decreases if the volume fraction of water is increased to 95%, and more so at 99% water. No change in the λ_{max} of emission is observed between the nanoparticles and dissolved species, unlike the monomeric silole amine nanoparticles which undergo a 10 nm red-shift in fluorescence relative to the dissolved species. This may indicate that the majority of the silole rings in the oligomer are protected from solvent, because of the helical structure.[7] This may also explain the much longer lifetime observed for the oligomer in solution (590 ps) as compared to the monomeric silole amine (26 ps).

Nanoparticles formed with higher water volume fractions ($\geqslant$80%) are quite stable. Fluorescence spectra taken on 6 mg L^{-1} nanoparticles stored in amber vials (to protect from photobleaching) showed little to no change (<5%) in fluorescence intensity over 5 days time.

Colloids of **1** consist of particles on the order of 80 nm in diameter, as determined by dynamic light scattering measurements.[14] Particle diameter appears to vary somewhat with water fraction, but to be more or less monodisperse ($\pm$20%) for any given suspension (Table 1).

Flourescence lifetimes[14] of the nanoparticles were measured and compared to those of the solid oligomer as well as to a THF solution of the oligomer. Three exponentials were needed to obtain

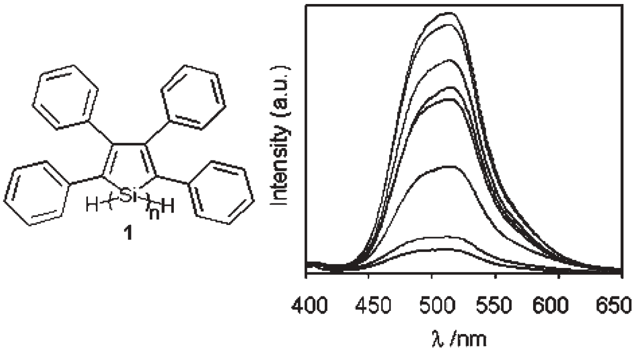

Fig. 1 Left: oligo(tetraphenyl)silole; right: fluorescence spectra of oligosilole aggregates in THF : H_2O suspensions with %H_2O, from top, equal to 90, 80, 95, 99, 70, 60, 50, and 0%.

Table 1 Summary of percent aggregated silole, particle diameter (D) mean lifetimes of emission (τ), and Stern–Volmer constants (K_{SV}), for nanoparticle suspensions of **1** (6 mg L^{-1}) at various water percentages

% H_2O	% Aggregates	D/nm	τ/ns	K_{SV}
0[a]	<1	—	0.590	970
50	3	—	0.625	2800
60	30	90	1.43	3400
70	55	90	2.48	3300
80	>95	70	3.64	5000
90	>95	60	3.84	4100
95	>95	70	3.48	4300
99	>95	100	3.26	4500

[a] In THF.

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an adequate fit of the fluorescence decay. The oligomers exhibit a trimodal distribution of molecular weights[15] and are not expected to respond as a single chromophore. In addition, the nanoparticles vary somewhat in size. Even a 20–30% variation in diameter amounts to a 170–220% change in volume and, potentially, a 290–480% variation in the duration of random energy migrations to quenching sites. The distribution of quenching sites may show heterogeneity itself. Even the solid oligomer with a mean lifetime of 4.08 ns does not follow a single exponential decay, indicating the possibility of multiple decay pathways in the oligomer chain.

Mean lifetimes[16] also depend on the water fraction in the suspensions (Fig. 2). The mean lifetime of oligosilole nanoparticles in 90% water have the longest lifetime, 3.84 ns, followed by the 80, 95, and 99% water suspensions (Table 1). This trend follows the steady state fluorescence, in that the more intensely luminescent samples are longer lived. The large difference in mean lifetime between 50% water (0.625 ns) and 60% water (1.43 ns) further supports the conclusion that 60% water is the onset of aggregation, as suggested by the steady state fluorescence changes (Fig. 1).

The percentage of silole existing in the suspension as aggregates was calculated from the fluorescence lifetime decay curves (Table 1). The nonexponential fluorescence decay from the unaggregated polymer is not easily distinguished from the fluorescence decay of the aggregates, imposing some limit on the certainity of the fit. Only 3% of silole is aggregated at 50% water, but the value rises to 30% at 60% water, coinciding with the rise in luminescence at these water fractions. Nearly all (>95%) of the silole is aggregated for suspensions consisting of 80% water and above. The decay curves of 80% water and above are essentially identical with the decay curve for the solid silole, demonstrating that most or all of the silole in the suspension is aggregated.

The lower fluorescence yields of the 95% and 99% water suspensions may be due to the kinetics of aggregation in the precipitation of the colloids. It is possible that during rapid precipitation with large amounts of water, solvent is trapped within the particles. This would account for the larger particle sizes observed, as well as the slightly shorter lifetimes observed. The behavior of this system is in contrast to the silole amine nanoparticle suspensions,[4] whose large increase in luminescence for 95% and 99% water fraction colloids correlates with a higher percentage of the silole being precipitated as nanoparticles at these higher water fractions.

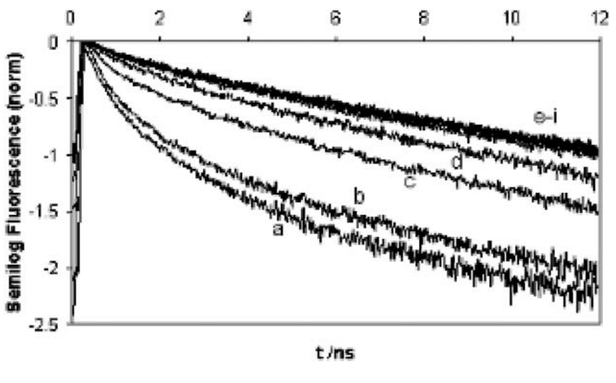

Fig. 2 Semilog plots of fluorescence decay *versus* time for nanoparticle suspensions in (a) 0%, (b) 50%, (c) 60%, (d) 70%, (e) 80%, (f) 90%, (g) 95%, (h) 99% water, and (i) solid oligosilole.

The ability of the oligosilole nanoparticles to detect TNT through luminescence quenching was investigated by adding successive aliquots of a THF stock solution of TNT to the nanoparticles. The decrease in luminescence was monitored as a function of added TNT. Luminescence quenching is observed as low as 100 ppb in pH 7 buffered solution. The response to quenching of various colloids was analyzed using the Stern–Volmer equation:[17,18] $I_0/I = K_{SV}[Q] + 1$.

Linear Stern–Volmer relationships are observed for both the colloidal and solvated oligosilole in the ppm range. Linear relationships may arise from either a static or dynamic quenching mechanism. In the case of dynamic quenching, bimolecular collisions of the quencher and fluorophore occur; hence, lifetimes vary proportionally with quencher concentration. In the case of static quenching, quenching occurs through a bound complex of quencher and fluorophore, and lifetimes are invariant with quencher concentration.[19] Fluorescence lifetimes of nanoparticle suspensions of various water percentages were measured and were largely unchanged by added TNT (Fig. 3). This indicates a static quenching mechanism, as previously observed for TNT and oligosilole in toluene solution.[7] It was hypothesized that the planar TNT molecule intercalates between the phenyl substituents around the silole ring, a mechanism which may likewise account for the static quenching of the oligosilole nanoparticles. Since intercalation may upset aggregate structure, especially at high quencher concentration, there may be small changes in excitation migration through the aggregates that is reflected by the small changes in lifetimes observed at high TNT concentration.

The Stern–Volmer analysis also allows a comparison of the quenching efficiencies of TNT on the various colloids (Fig. 4). Quenching experiments were performed on nanoparticle suspensions, as well as on **1** dissolved in THF. Quenching efficiencies improved more than 400% for the nanoparticles relative to the dissolved oligosilole (Table 1). The K_{SV} were similar for nanoparticle suspensions consisting of a minimum of 80% water, which is consistent with their similar size and lifetime. At water percentages below 80%, when the silole is not significantly aggregated, quenching efficiencies drop noticeably. Thus, aggregation to form nanoparticles is favorable for TNT detection in aqueous solution.

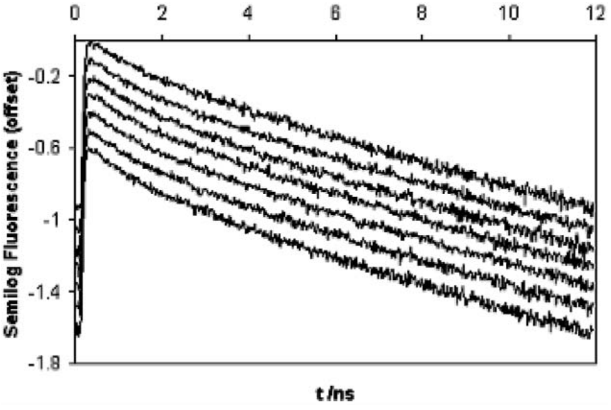

Fig. 3 Semilog plots of fluorescence decay *versus* time for a nanoparticle suspension of **1** in 90% water with, from top, 0, 2, 4, 6, 8, 10, and 20 ppm added TNT. Curves have been offset for clarity.

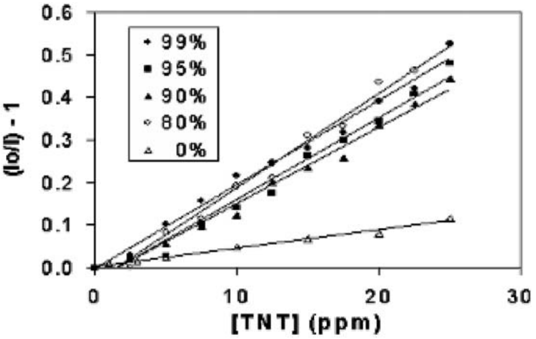

Fig. 4 Stern–Volmer plots of luminescence quenching of nanoparticle suspensions of **1** in various water percentages by TNT.

In the case of static quenching, the Stern–Volmer constant (K_{SV}) is an association constant between the quencher and fluorophore receptor sites. It was found that vigorous shaking or stirring of the colloid after addition of TNT more than doubled the quenching efficiency. Such bulk mixing of the sample may aid in the adsorption of analyte into polymer. Under these conditions, quenching comparable to the sensitivity of commercially available colorimetric kits is easily observed below 20 ppb.

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