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Kinetic trapping of host–guest complexes in a polymeric matrix

Faysal Ilhan, Laura Diamondis, Leigh Gautreau and Vincent M. Rotello*

Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA. E-mail: rotello@chem.umass.edu

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Diaminotriazine–flavin host–guest complexes are kinetically trapped in spin-cast polystyrene films.

Self-assembly is a powerful tool for the creation of nanoscale constructs. These non-covalently assembled host–guest complexes have been used to fabricate many molecular-scale components such as wires,[1] switches[2] and computers.[3] Central to the pragmatic utilization of these constructs, however, are the issues of immobilization and isolation. These attributes allow the utilization of molecular components to fabricate useful devices from the disorganized ensemble of components present in the solution phase.

Polymer matrix isolation is an effective technique for the isolation and immobilization of molecules.[4] Application of this methodology to the isolation of host–guest assemblies is hampered by issues of competition and aggregation. Matrix formation from polar polymers creates a competitive environment, disrupting the desired interactions such as hydrogen bonding. Conversely, creation of matrices using non-polar polymers can cause aggregation and concomitant phase separation of polar host–guest complexes. To overcome the issue of phase separation in non-polar polar matrices, we have explored methods of trapping host–guest complexes. We report here, the kinetic isolation of individual hosts and host–guest complexes in a highly non-polar polystyrene matrix through spin-casting of polymer solutions.

In preliminary investigations, we explored the fluorescence behavior of flavin **1** in different volumes of polystyrene films. The polymer-doped films were prepared by spin-casting[5] from solutions of 0.41, 0.87 and 1.75% w/w polystyrene ($M_n = 1{,}1 \times 10^5$, PDI = 2.3) and varying quantities of flavin **1**[6] in $CHCl_3$ on SiO_2 surfaces.[7] The optical transparency of these films[8] allowed direct observations of flavin **1** fluorescence behavior.[9] Addition of more equivalents of flavin **1** resulted in an increased quenching of fluorescence emission for the films prepared from solutions of 0.41 and 0.87% w/w polystyrene in $CHCl_3$ (Fig. 1).[10] This behavior is diagnostic of self-aggregation of flavin **1**. For films prepared from a solution of 1.75% w/w polystyrene in $CHCl_3$, increasing concentrations of flavin **1** resulted in a linear increase in fluorescence emission, demonstrating that self aggregation was effectively suppressed (Fig. 2). Heating of these films to temperatures higher than the T_g of the polystyrene (*ca.* 398 K) resulted in marked reduction in fluorescence and curvature of the fluorescence *vs.* concentration plot, both behaviors diagnostic of flavin aggregation.

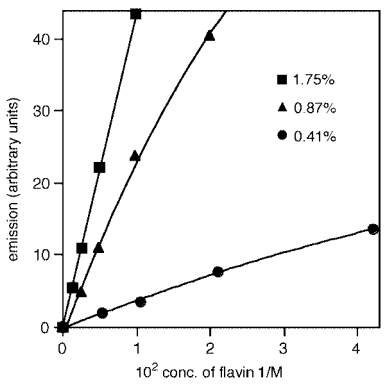

Fig. 1 Plot of fluorescence emission *vs.* concentration of flavin **1** in films prepared from solutions of 0.41, 0.87 and 1.75% w/w polystyrene in $CHCl_3$. Excitation: 445 nm, emission: 525 nm.

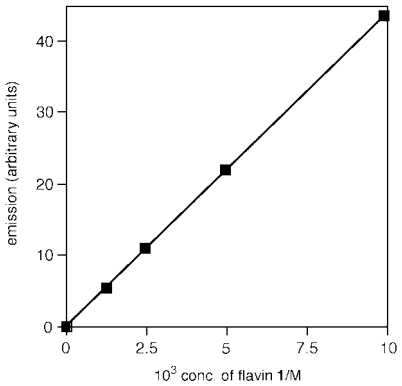

Fig. 2 Plot of fluorescence emission *vs.* concentration of flavin **1** in films prepared from a solution of 1.75% w/w polystyrene in $CHCl_3$. Excitation: 445 nm, emission: 525 nm.

To explore the complexation of flavin **1** *via* hydrogen bonding in the non-polar polystyrene matrix, films containing flavin **1** and complementary diaminotriazine-based[11] guest **2** were prepared. As shown in Fig. 3, increasing quantities of guest **2** resulted in only slightly decreased flavin **1** fluorescence emission for films prepared from solution of 0.41% w/w polystyrene in $CHCl_3$. This is consistent with non-specific aggregation between flavin **1** and triazine **2**. In contrast, titrations with 1.75% w/w polystyrene films showed marked decreases in fluorescence of flavin **1** with increasing concentrations of receptor **2**, reaching a limiting value. This is concordant with solution based investigations, where we established that hydrogen bonding between flavin **1** and guest **2** effectively quenches flavin fluorescence (Fig. 4).[12] Control experiments utilizing N(3)-methyl flavin **3** (Fig. 5), a molecule not capable

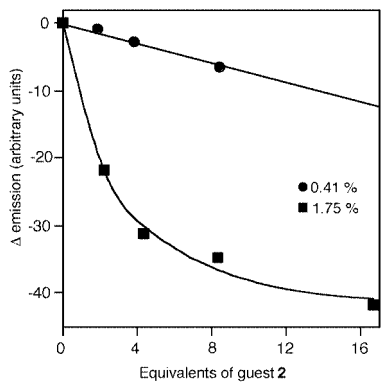

Fig. 3 Fluorescence emission changes of flavin **1** upon addition of triazine **2** in films prepared from solutions of 0.41 and 1.75% w/w polystyrene in $CHCl_3$. Excitation: 445 nm, emission: 525 nm. The curve for the titration performed with 1.75% w/w polystyrene films represents the best fit to the 1:1 binding isotherm. The line for the titration performed with 0.41% w/w polystyrene is a linear fit to the data points, and is intended only as a guide to the eye.

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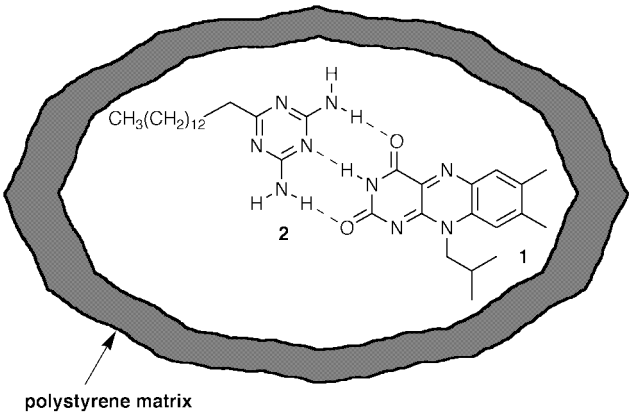

Fig. 4 Schematic illustration of isolated flavin **1**–triazine **2** host–guest complexes in a polystyrene matrix.

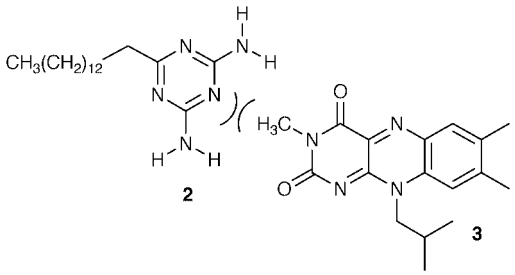

Fig. 5 N(3)-methyl flavin **3**–guest **2**.

of complementary binding through hydrogen bonding, in place of host **1** did not demonstrate any measurable complexation with guest **2**.

After calculating the volume of polymer matrices, the apparent association constants for flavin **1**–triazine **2** complexation were estimated by fitting the data to 1 : 1 binding isotherms for each different titration set of films. We did not observe any quantifiable recognition between flavin **1** and triazine **2** in films prepared from 0.41% w/w polystyrene solution, as a result of flavin **1** aggregation. For the films prepared from 1.75% w/w polystyrene solution, an estimated binding constant of 53 ± 12 M^{-1} was obtained.[13] This is considerably lower than the binding constant of 555 ± 8 M^{-1} which was obtained for the same host–guest complex formation in $CHCl_3$,[14] despite the non-competitive nature of the forming polystyrene matrix. This reduction in binding constant can be attributed to both the development of stress during polymer film formation[15] and the polymer entanglement during the deposition process, issues that we are currently exploring.

In summary, we have demonstrated the kinetic isolation of individual host flavin **1** and host flavin **1**–guest triazine **2** complexes in a highly non-polar polystyrene matrix through spin-casting of polymer solutions. Self-aggregation of polar flavin **1** in these non-polar polymer films was prevented by adjusting the ratio between polystyrene and flavin **1** in solution prior to spin casting. Fundamental and applied studies of this approach are underway and will be reported in due course.

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8 The polymer-doped films were highly transparent. For example, the film of 1.75% w/w polystyrene containing 1×10^{-2} M flavin **1** showed 96% transmittance at 445 nm.

9 Fluorescence measurements were performed using a machined slide holder. The slides were vertically set, with the polymer coated surface at an angle of 60° to the excitation beam.

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