Supplementary Information

Selective Encapsulation of Dye Molecules in Dendrimer/polymer Multilayer Microcapsules by DNA Hybridization

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Figure S1. Chemical structure of globular $N,N$-disubstituted hydrazine phosphorus-containing dendrimers of the fourth generation having 96 terminal groups with cationic (G4$^+$).
Figure S2. Using planar Au model substrates coated with 3-mercaptopropionic acid (3-MPA). To this end, we consecutively deposited multilayers of G$_4^+$ dendrimers (1 mg/mL) and PSS (1 mg/mL, 0.5 M NaCl). The resulting kinetic mode SPR curve is shown in Fig. S2a. The addition of each layer led to a regular increase of the reflectivity. The accumulated shift of the resonance angles was converted into the geometrical film thickness by assuming a refractive index of $n \approx 1.5$ for the PSS and G$_4^+$ (Fig. S2b). [Kim, D. H.; Hernandez-Lopez, J. L.; Liu, J. Y.; Mihov, G.; Zhi, L. J.; Bauer, R. E.; Grebel-Kohler, D.; Klapper, M.; Weil, T.; Mullen, K.; Mittler, S.; Knoll, W. *Macromol. Chem. Phys.* **2005**, *206*, 52-58.] The mean increase in the thickness of the multilayer system was determined to be $\Delta d \approx 2.1$ nm for an additional PSS layer and $\Delta d \approx 4.1$ nm for an additional G$_4^+$ layer.
DNA Immobilization and Hybridization Studied by SPFS:

The selective encapsulation of Cy5 molecules by specific interaction between P2 and Cy5T2 was further studied by surface plasmon field-enhanced fluorescence spectroscopy (SPFS) technique, an approach typically for studying DNA hybridization (E. Kretschmann, Z. Phys. 1971, 241, 313-324). Firstly, Au substrate coated with a mercaptoundecanoic acid (MUA) monolayer was prepared. The monolayer was activated by immersion in PBS solution of 1-ethyl-3-(dimethylamino)-propylcarbodiimide (EDC; 1 mol/l) and N-hydroxysuccinimide (NHS; 0.2 mol/l) (C. L. Feng, et.al. Advanced Materials 2007, 19, 286-290.). In order to graft P2 on the monolayer by the formation of covalent bond, amino-functionalized P2 was selected and immobilized from a 1 μM aqueous solution (PBS, pH = 7.4) by amide bond formation. The kinetic increase of the optical thickness with time is shown in Fig. S3a. It shows that the reaction between amino group functionalized P2 and MUA monolayer is very rapid at the early stage and P2 adsorption reaches equilibrium in PBS solution after 10 min. With rinsing by PBS, a low dissociation speed is observed, suggesting a successful immobilization of P2 on the monolayer.

After P2 immobilization on Au substrate, the aqueous solution containing Cy5Tmm and Cy5T2 (pH = 7.4) was applied to the surface, respectively. Firstly, the injection of Cy5Tmm can be seen as a small jump of fluorescence intensity originating from Cy5 being excited by the residual transmitted and the elastically scattered laser beam (Fig. S3b). Switching back to pure buffer leads to a fast decrease of the low fluorescence intensity with a very slow further decrease. However, upon the addition of the solution with Cy5T2 the fluorescence intensity rises very rapidly and reaches a much high fluorescence level (Fig. S3b). A relatively fast decrease of the fluorescence intensity is observed at the early stage if rinsing with pure buffer. Rinsing affects the intensity only very little and leads to a very slow decrease with time. The results demonstrate that the interaction between P2 and T2 show very high selectivity by hybridization.

Figure S3. a) P2 immobilization on MUA monolayer investigated in situ by SPR (kinetic scan). b) Kinetic fluorescence scans taken for hybridization and dissociation processes between P2 and Cy5Tmm (1) and Cy5T2 (2) under the excitation at the wavelength of 632 nm.