# Interrupted Energy Transfer: Highly Selective Detection of Cyclic Ketones in the Vapor Phase

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**S** *Supporting Information*

**ABSTRACT:** We detail our efforts toward the selective detection of cyclic ketones, e.g. cyclohexanone, a component of plasticized explosives. Thin films comprised of a conjugated polymer are used to amplify the emission of an emissive receptor via energy transfer. We propose that the energy transfer is dominated by an electron-exchange mechanism to an upper excited state of the fluorophore followed by relaxation and emission to account for the efficient energy transfer in the absence of appreciable spectral overlap. Exposure to cyclic ketones results in a ratiometric fluorescence response. The thin films show orthogonal responses when exposed to cyclic ketones versus acyclic ketones. We demonstrate that the exquisite selectivity is the result of a subtle balance between receptor design and the partition coefficient of molecules into the polymer matrix.

**Figure 1.** (a) Synthesis of squaraine reporter dye **1**. (i) 3,5-Bis-(trifluoromethyl)phenyl isocyanate, $CH_2Cl_2$, rt, 12 h. (ii) Squaric acid, toluene/*n*-butanol (3:1), reflux, 6 h. (b) Molecular structure of PPE **2** (R = $C_{14}H_{29}$). (c) Absorbance (solid line) and photoluminescence (circles) spectra of PPE **2** (blue) and squaraine **1** (red). PPE **2** photoluminescence spectra are from a thin film; all other measurements taken in $CHCl_3$ (**2** $\lambda_{ex}$ = 380 nm, **1** $\lambda_{ex}$ = 660 nm). The red shift of the emission maximum of **1** in thin films is likely due to stabilization of the excited state of **1** in the polymer matrix.

D espite significant advances in fluorescence-based chemosensing technology,[1] the detection of energetic materials remains an important area of research. Recent events worldwide have highlighted the need for a portable and highly sensitive explosives sensing device capable of high-throughput screening in a variety of environmental conditions.[2] However, explosive compositions containing 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) remain particularly challenging targets. Indeed, a low equilibrium vapor pressure of 6 ppt at 25 °C and an unfavorable reduction potential add to the complexity of this problem.[2,3] To address this need, we focused our efforts on the detection of cyclohexanone, a ketone used in the recrystallization of RDX with an equilibrium vapor pressure of 4470 ppm.[4] However, optical detection of cyclohexanone vapor in an operational environment is not without its own challenges; specifically, the ubiquity of ketones in nature requires a highly selective sensing system. This Communication describes a new approach to this goal.

Our transduction mechanism, predicated on interrupted electronic energy transfer (EET), is schematically outlined in Figure 1d. A stable and highly emissive conjugated polymer (**2**) is used as a light-harvesting unit to amplify the emission from a fluorophore (squaraine **1**) embedded in a thin film via EET. Two primary mechanisms exist for singlet—singlet energy transfer, a long-range dipole—dipole interaction commonly referred to as Förster resonance energy transfer (FRET)[5] and an electron-exchange pathway formulated by Dexter.[6] Figure 1c shows the absorb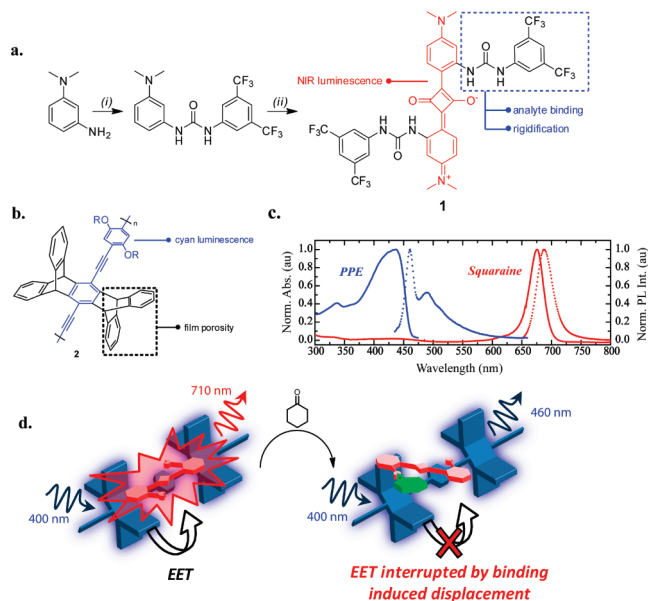ance and photoluminescence data for both components used in this work. The conjugated polymer emission displays negligible spectral overlap with the squaraine absorbance even in thin films. However, closer inspection of the dye absorbance reveals a small transition centered at ~415 nm. This transition has been observed in other squaraine systems and has been attributed to an $S_0 \rightarrow S_n$ excitation as the $S_0 \rightarrow S_2$ is forbidden by symmetry.[7] Given that the efficiency of FRET processes are dependent on the oscillator strength of the coupled transitions, and exchange processes are not,[8] we propose that the observed energy transfer process consists of an electron exchange from the excited polymer to the $S_n$ state of the squaraine followed by rapid relaxation to the $S_1$ state and subsequent emission. It must be noted, however, that in thin films both mechanisms are
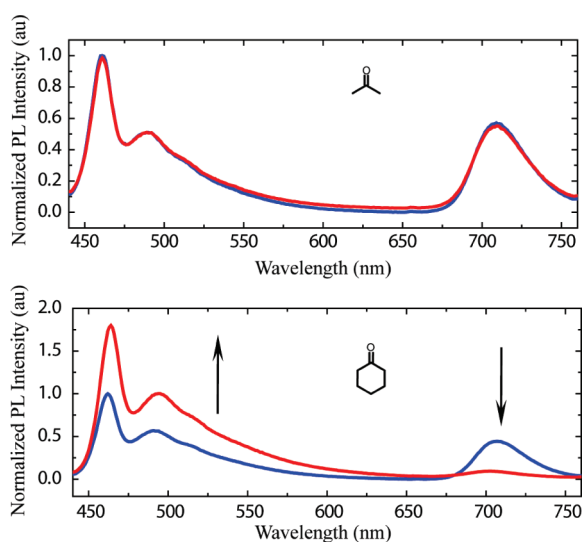
**Figure 2.** Thin-film fluorescence spectra before (blue) and after (red) exposure to the saturated vapor of acetone (top) and cyclohexanone (bottom) for 30 s ($\lambda_{ex}$ = 400 nm).



**Figure 3.** Change in thin-film fluorescence intensity of polymer (blue) and squaraine dye (red) after 30 s exposure to the saturated vapor of the indicated ketone ($\lambda_{ex}$ = 400 nm)(mean of three different films).



**Figure 4.** Mean frequency shift of a QCM crystal coated with a thin film of the sensor formulation after 30 s exposure to the saturated vapor of the indicated ketone (mean of three sequential measurements).

potentially operative given such small separations between the donor and acceptor.[9] Given the negligible spectral overlap between the two components in this work and the fact that there is a finite overlap in the absorbance of both components, the energy transfer cascade is more consistent with an exchange mechanism.[8−10] Of critical importance to this work is the fact that the efficiency of energy transfer, by an exchange mechanism, should be extremely sensitive to intermolecular distance changes of only a few angstroms.[8−11] Herein, we report that ratiometric and selective detection of ketones can be realized using rationally designed acceptor molecules that modulate energy transfer efficiency based on binding-induced displacement of the acceptor from the conjugated polymer backbone.

The key feature of this approach is the ability to detect analytes lacking low-lying electronic states that do not alter the electronic properties of either the donor or acceptor and also do not undergo photoinduced electron transfer (PET) with either component. Instead, binding interactions between the analyte and dye cause small molecular movements (0.5−2 Å) that diminish orbital interactions (or modulate the orientation) between the dye and luminescent polymer backbone, yielding a quench in the reporter dye emission and a concomitant increase in the conjugated polymer emission.

The synthesis of squaraine **1** is outlined in Figure 1a. A urea based receptor was chosen due to the extensive use of this motif in organocatalysis[12] involving carbonyl-containing substrates, and was linked to a near-infrared (NIR) squaraine fluorophore in a fashion that enables the formation of a strong intramolecular hydrogen bond. This interaction rigidifies the dye scaffold thereby increasing the quantum yield of the fluorophore and enhances the efficiency of energy transfer by limiting nonradiative decay pathways.[13] In addition, the rigidity between the receptor periphery and the fluorophore core ensures that a binding event will displace the core from the polymer backbone. The resulting acceptor dye **1** undergoes facile energy transfer when colocalized in a thin film of poly($p$-phenylenethynylene) (PPE) **2** at a dye loading of 0.5 wt % as shown in Figure 2 (rationale for this dye loading is discussed in the Supporting Information).
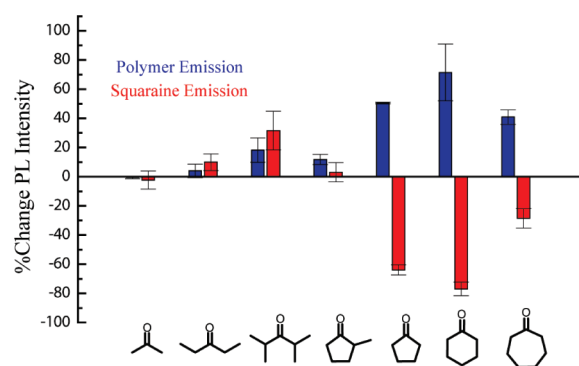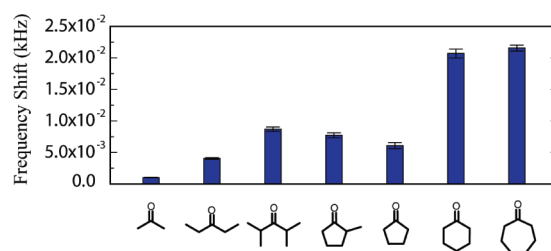
Exposure of these films to the saturated vapor of hydrogen-bond acceptors such as cyclohexanone results in a pseudoratiometric 'polymer-on'/'dye-off' response (Figure 2). Interestingly, the films do not elicit the same response when exposed to the saturated vapors of acyclic ketones such as acetone. This result was surprising to us as we anticipated that acetone would elicit a much larger response given its compact size and volatility. Exposure to other acyclic ketones such as 3-pentanone and diisopropyl ketone also behaved differently than cyclohexanone. In fact, the emission intensity of both components tends to increase to a small degree (5−30%) when exposed to these vapors (Figure 3). This response can be explained by a swelling mechanism whereby the ketones swell the conjugated polymer film and reduce interpolymer $\pi-\pi$ interactions that act as nonemissive low-energy exciton traps. These excitons are then free to migrate to sites bearing squaraine molecules and undergo energy transfer followed by emission.

Exposure to other cyclic ketones such as cyclopentanone and cycloheptanone gave responses similar to cyclohexanone. We initially suspected that the observed selectivity may be due to differential uptake of the analytes into the hydrophobic polymer matrix. To test this hypothesis, a quartz crystal microbalance (QCM) was used to measure the change in frequency of the oscillating quartz crystal (coated with the polymer matrix) upon exposure to various analytes (Figure 4). The resulting frequency changes are linearly related to the uptake of mass into the films by Sauerbrey's equation.[14] We expected the ratiometric response of the films to trend in the same manner as the partition coefficients of the different analytes.

As shown in Figures 3 and 4, this hypothesis is in line with the observed response of the films to acyclic ketone vapor. Clearly,
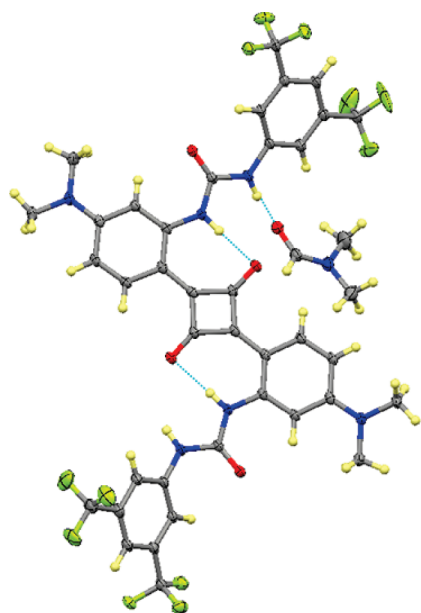
**Figure 5.** X-ray structure of **1** (1:1 cocrystal with DMF) (gray = carbon, green = fluorine, blue = nitrogen, red = oxygen, yellow = hydrogen, light blue dashed lines = hydrogen bonds).

the swelling response of the films in Figure 3 follows the same trend as the frequency shifts shown in Figure 4. However, this hypothesis fails to explain the disparate response between cyclopentanone and diisopropyl ketone. Additionally, one would expect the largest response from cycloheptanone (with the greatest relative uptake into the films); however, the films display a greater response to cyclopentanone and cyclohexanone. These data lend credence to two important conclusions: (1) the receptor is involved in the proposed transduction mechanism —the response for cyclic ketones is not the result of film swelling —and (2) the observed selectivity is related to the steric bulk surrounding the ketone functionality and the partition coefficient of the analyte into the film.

To further probe these points, we investigated the response of the films to 2-methylcyclopentanone. We expected that if the selectivity was related to steric bulk in the vicinity of the carbonyl functional group, then the sensor should behave differently in the presence of 2-methylcyclopentanone versus cyclopentanone. In accord with our hypothesis, the response to the two analytes is orthogonal (Figure 3), despite having very similar uptake profiles into the polymer films (Figure 4). This result supports both the notion that the receptor is involved in the selectivity of the response and that the binding pocket of squaraine **1** requires sterically unhindered ketone functionalities to induce a ratiometric response.

The crystal structure of squaraine **1** is shown in Figure 5. Of particular note is the small binding cavity created by the aryl $CF_3$ groups and the oxygen functionality attached to the central four-membered ring. It appears that this cavity is well suited for cyclic ketones, with their 'pinned back' alkyl substituents, and endows the receptor with a high level of selectivity.

In summary, a conceptually new approach to the selective detection of cyclic ketones has been demonstrated. This approach makes use of the light harvesting ability of conjugated polymers to amplify the emission from embedded fluorophores as well as the strong distance dependence of exchange based

energy transfer mechanisms. The resulting films display exquisite selectivity for cyclic ketones, including cyclohexanone which is a component of plasticized explosives. The selectivity appears to be due to a subtle balance of receptor specificity and the ability of analytes to partition into the polymer matrix. These films exhibit a limit of detection for cyclohexanone of 4.76 ppm.[15] Further investigations of this approach and its utility in explosives detection are currently underway in our laboratory.

## ■ ASSOCIATED CONTENT

**ⓢ Supporting Information.** Experimental details including synthetic procedures, characterization of all compounds, and spectral data for the quenching experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

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## ■ ACKNOWLEDGMENT

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