

Base-Catalyzed Ship-in-a-Bottle Synthesis of a Prefluorescent, Zeolite-Incorporated Sensor for Monitoring Radical Processes in Zeolites

Andrea Ricci, Michelle N. Chrétien, and J. C. Scaiano*

Department of Chemistry, Center for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie, Ottawa K1N 6N5, Ontario, Canada

Received January 10, 2004. Revised Manuscript Received April 19, 2004

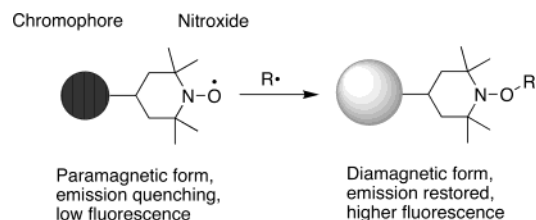
Prefluorescent probe dansyl-TEMPO was synthesized within NaY supercages by means of a base-catalyzed ship-in-a-bottle synthesis to yield the supramolecular assembly DT@NaY, providing the first example of base-catalyzed synthesis in the normally acidic zeolite cavities. This material was successfully employed in the solid state as a sensor to monitor intercavity diffusion of carbon-centered radicals produced by AIBN thermolysis and in a slurry to study the interpore diffusion of carbon-centered radicals produced in solution from a suitable precursor (3,3'-diphenyl-3H,3'H[3,3']bibenzofuranyl-2,2'-dione, **6**). The dynamics of hydrogen atom transfer from a good donor, such as the synthetic lactone antioxidant 3-phenyl-2-coumaranone, to DT@NaY were also investigated in benzene slurry.

Introduction

The application of prefluorescent probes for the detection of carbon-centered radicals is a topic of current research interest. Originally reported by Blough and co-workers,^{1,2} prefluorescent probes are dual-function molecules consisting of a fluorophoric unit tethered to a stable nitroxyl radical (such as 2,2,6,6-tetramethylpiperidine-1-oxyl radical, TEMPO). In the paramagnetic form (Scheme 1), the excited singlet state of the fluorophore is efficiently quenched by the tethered nitroxide. The details of excited-state quenching are dependent on the particular chromophore–nitroxide pair and may comprise contributions from several possible mechanisms² including electron-exchange-induced intersystem crossing or internal conversion, energy transfer via Förster or Dexter mechanisms, and electron transfer. There are examples in the literature where the mechanism has been elucidated for specific fluorophore–nitroxide pairs.^{2–4}

It is well-known that stable nitroxides are highly active scavengers of carbon-centered radicals,^{5–8} when the nitroxide moiety of a prefluorescent probe couples with a carbon-centered radical (R• in Scheme 1) the

Scheme 1. Detection Mechanism of Prefluorescent Probes



result is a diamagnetic alkoxyamine. After radical trapping the fluorescence-quenching mode operative in the paramagnetic probe is no longer available and the fluorophore emission is restored. The radical detection ability of a prefluorescent probe is a consequence of the different fluorescence quantum yields for the diamagnetic and paramagnetic forms; by measuring the time evolution of the fluorescence intensity, various prefluorescent probes have been employed to obtain kinetic information for reactions involving carbon-centered radicals.^{9–14}

In recent years our research group has been very active in the design of new probes as well as in the investigation of novel applications for this fluorescence-based detection methodology. Most of this work has been carried out using QT (4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, **1**), a prefluorescent probe with quinoline as the

* To whom correspondence should be addressed. E-mail: tito@photo.chem.uottawa.ca.

(1) Blough, N. V.; Simpson, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 1915–1917.

(2) Green, S. A.; Simpson, D. J.; Zhou, G.; Ho, P. S.; Blough, N. V. *J. Am. Chem. Soc.* **1990**, *112*, 7337–7346.

(3) Green, S. A.; Fox, M. A. *J. Phys. Chem.* **1995**, *99*, 14752–14757.

(4) Herbelin, S. E.; Blough, N. V. *J. Phys. Chem. B* **1998**, *102*, 8170–8176.

(5) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992–4996.

(6) Chateaufneuf, J.; Luszytyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629–1632.

(7) Beckwith, A. L.; Bowry, A. L.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4.

(8) Skene, W. G.; Scaiano, J. C.; Listigovers, N. A.; Hazmaier, P. M.; Georges, M. K. *Macromolecules* **2000**, *33*, 5065.

(9) Gerlok, J. L.; Zacmanidis, P. J.; Bauer, D. R.; Simpson, D. J.; Blough, N. V. *Free Radical Res. Commun.* **1990**, *10*, 119–121.

(10) Kieber, D. J.; Blough, N. V. *Free Radical Res. Commun.* **1990**, *10*, 109–117.

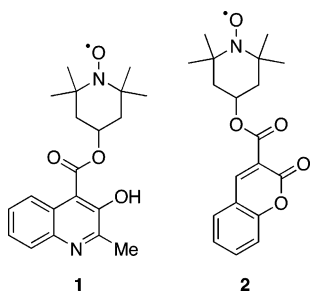
(11) Kieber, D. J.; Blough, N. V. *Anal. Chem.* **1990**, *62*, 2275–2283.

(12) Li, B.; Gutierrez, J. P. L.; Blough, N. V. *Anal. Chem.* **1997**, *69*, 4295–4302.

(13) Moad, G.; Shipp, D. A.; Smith, T. A.; Solomon, D. H. *J. Phys. Chem. A* **1999**, *103*, 6580–6586.

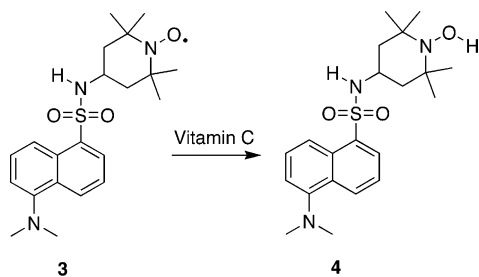
(14) Pou, S.; Huang, Y. I.; Bhan, A.; Bhadti, V. S.; Hosmane, R. S.; Wu, S. Y.; Cao, G. L.; Rosen, G. M. *Anal. Biochem.* **1993**, *212*, 85–90.

fluorescent moiety. QT has been successfully applied to the study of various systems including the thermal¹⁵ and photochemical¹⁶ generation of carbon-centered radicals in polymer films, radical evolution during TiO₂-mediated photodegradation of SDS micelles,¹⁷ and photodecomposition of dibenzyl ketone within zeolites.¹⁸ Similarly, a coumarin-based prefluorescent probe (**2**) has been employed to monitor the kinetics of end-cap cleavage in TEMPO-mediated living free radical polymerization.¹⁹ We report here on the ship-in-a-bottle synthesis of the prefluorescent probe dansyl-TEMPO (4-(5-(dimethylamino)-1-naphthalenesulfonylamido)-2,2,6,6-tetramethylpiperidine-1-oxyl, **3**) inside faujasite NaY (DT@NaY) and its application for monitoring dynamic radical processes occurring within the microheterogeneous system of NaY supercages.



Dansyl-TEMPO (DT, **3**) has been previously employed by Likhtenshtein et al. for the quantitative analysis of vitamin C in biological liquids such as commercial fruit juices.²⁰ The fluorescence increase observed in this case was a result of hydrogen atom transfer from vitamin C, a good hydrogen donor, to the nitroxide moiety yielding the corresponding diamagnetic hydroxylamine **4** (Scheme 2). Notably, the high fluorescence quantum

Scheme 2. Reaction of Vitamin C with DT (4-(5-(Dimethylamino)-1-naphthalenesulfonylamido)-2,2,6,6-tetramethylpiperidine-1-oxyl, **3)**



yield of dansylamines is not completely quenched by nitroxyl moieties; the paramagnetic form of DT possesses a significant fluorescence emission and the intensity difference between the diamagnetic and paramagnetic forms of DT has been reported to be a factor

of ca. 2.²⁰ When prefluorescent probes are used in solution it is normally preferable to have a large difference between the fluorescence emission of the free and trapped probe (usually between 30- and 60-fold).^{1,2,5-19} In this sense DT is less than ideal; however, in the present case we chose DT for our study because the weak fluorescence emission from its paramagnetic form was a direct and convenient tool to establish the formation of the prefluorescent probe inside the zeolite.

Results and Discussion

Synthesis of DT@NaY. In the investigation of dynamic radical processes taking place within NaY (either in the solid state or in solvent slurries), one important goal is the immobilization of the prefluorescent probe inside the cavities of NaY to prevent its own diffusion as radicals migrate through the microheterogeneous system. This is even more important when monitoring the diffusion of radicals generated from a precursor located in the solution phase of a zeolite/solvent slurry. In the latter case, segregation of the probe also prevents it from exiting NaY in the presence of the solvent.

In light of these considerations, probe segregation was achieved by employing ship-in-a-bottle synthesis, an inventive strategy designed for the preparation of inclusion complexes of bulky molecules which can be accommodated in the 13-Å supercage of NaY, but cannot penetrate the 7.4-Å entrance windows.²¹ In this methodology, the smaller precursors are first included in the zeolite cavity where they subsequently undergo reaction to give the final product, which remains segregated as a result of its molecular dimensions. Dansyl-TEMPO is an ideal candidate for ship-in-a-bottle synthesis because its molecular dimensions are ca. 12–13 Å (i.e., it will be perfectly accommodated within the cage although its direct inclusion in NaY is impossible) while the probe's building blocks (TEMPO and the dansyl chromophore) are approximately 7 Å and therefore smaller than the cage window, through which they easily diffuse.

A base-catalyzed synthetic route to dansyl-TEMPO has previously been reported in the literature (Scheme 3);²² DT is easily obtained by treatment of 4-amino TEMPO, **5**, with dansyl chloride, **6**, at room temperature under anhydrous conditions (in pure pyridine or pyridine/dichloromethane mixtures). The same building blocks were employed for the synthesis in NaY. To the best of our knowledge this base-catalyzed ship-in-a-bottle synthesis is unique in the literature. Typical synthetic strategies are acid-catalyzed^{21,23} or metal-ion templated, as is the case for encapsulated metallo-phthalocyanines.²⁴ To perform a base-catalyzed ship-in-a-bottle synthesis pyridine was employed as a base to counteract NaY acidity. It has been established that organic bases are able to bind to the acidic sites in zeolite cavities, inducing pH modifications.^{25,26} For this reason, prior to the inclusion of dansyl chloride and

(15) Aspee, A.; Garcia, O.; Maretto, L.; Sastre, R.; Scaiano, J. C. *Macromolecules* **2002**, *36*, 3550–3556.

(16) Coenjarts, C.; Garcia, O.; Llauger, L.; Palfreyman, J.; Vinette, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 620–621.

(17) Ricci, A.; Maretto, L.; Chrétien, M. N.; Scaiano, J. C. *Photochem. Photobiol. Sci.* **2003**, *2*, 487–492.

(18) Aspee, A.; Maretto, L.; Scaiano, J. C. *Photochem. Photobiol. Sci.* **2003**, *2*, 1125–1129.

(19) Garcia Ballesteros, O.; Maretto, L.; Sastre, R.; Scaiano, J. C. *Macromolecules* **2001**, *34*, 6184–6187.

(20) Lozinsky, E.; Martin, V. V.; Berezina, T. A.; Shames, A. I.; Weis, A. L.; Likhtenshtein, G. I. *J. Biochem. Biophys. Methods* **1999**, *38*, 29–42.

(21) Scaiano, J. C.; Garcia, H. *Acc. Chem. Res.* **1999**, *32*, 783–793.

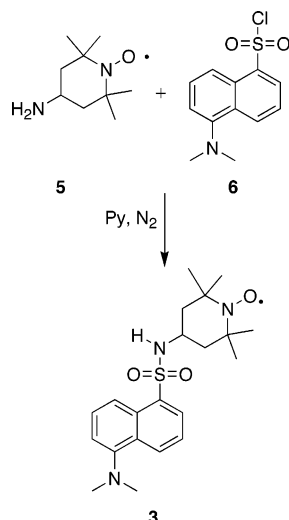
(22) Likhtenshtein, G. I.; Bogatyrenko, V. R.; Kulikov, A. V.; Hideg, K.; Hankovsky, H. O.; Lukoianov, N. V.; Kotelnikov, A. I.; Tanaschelchuk, B. S. *Dokl. Akad. Nauk. SSSR* **1980**, *253*, 4881–4484.

(23) Ward, J. W. *J. Catal.* **1968**, *10*, 34–36.

(24) Balkus, K. J. *J. Phthalocyanines* **1996**, *4*, 285–305.

(25) Scaiano, J. C.; Kalia, M.; Corrent, S. *J. Phys. Chem. B* **1997**, *101*, 8564–8568.

Scheme 3. Base-Catalyzed Synthesis of DT



4-amino TEMPO in NaY, the zeolite was pretreated with an excess of pyridine resulting in a sample with a final pyridine loading of $\langle S \rangle \sim 1$ (equivalent to one molecule per cavity). Following this pretreatment, 4-amino TEMPO and dansyl chloride were sequentially included in the zeolite in a one-pot procedure (to reach an occupancy of 0.5 for each) and the subsequent coupling reaction was carried out under nitrogen at room temperature (see Experimental Section for details). The zeolite was collected by filtration and washed several times with hexane and dichloromethane to remove any organic material present on the particle surface. TLC and HPLC analysis of the wash solution showed the presence of dansyl-TEMPO (assigned by comparison with an authentic sample of the probe, synthesized according to the reported procedure²²) along with pyridine and a mixture of unreacted dansyl chloride and 4-amino TEMPO. It is possible that, due to binding with acid sites, some pyridine may remain within the zeolite cavity but based on pyridine recovery after washing this is not significant. To confirm that the probe was effectively segregated inside the cavities, the solid sample was then subjected to exhaustive solid-liquid (Soxhlet) extraction with dichloromethane. After 1 day of extraction traces of dansyl-TEMPO were recovered; further treatment of the sample showed no evidence of probe extraction.

Unfortunately, dansyl-Tempo is not stable under strongly acidic conditions and therefore we could not directly confirm its formation within NaY cavities by analysis of the organic material recovered following acid degradation of the zeolite framework, a procedure that involves treatment of the inclusion complex with 4 M HCl followed by liquid-liquid extraction. The formation of DT@NaY was instead proven indirectly by analysis of various spectral data. The ground-state diffuse reflectance spectra acquired after solid-liquid extraction showed two bands (one centered at 330 nm and the other at 270 nm) which are in good agreement with the UV spectrum recorded of DT in acetonitrile solution (Figure 1).

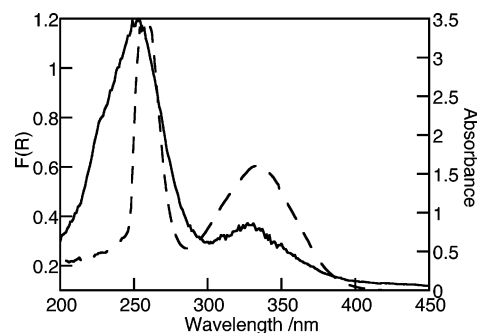


Figure 1. Comparison of the ground-state diffuse reflectance of DT@NaY (solid line) and the UV-Vis spectrum of DT in acetonitrile, [DT] = 5×10^{-4} M (dashed line).

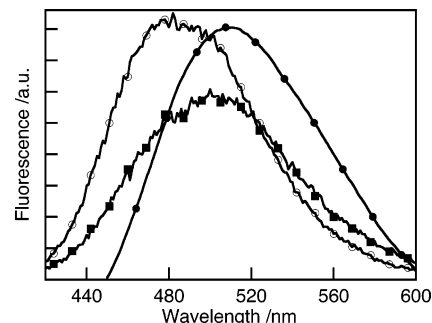


Figure 2. Fluorescence emission ($\lambda_{\text{ex}} = 330$ nm excitation) of a benzene solution of DT (1×10^{-4} M, $\lambda_{\text{max}} = 470$ nm, \circ), a solid DT@NaY sample ($\langle S \rangle = 0.1$, $\lambda_{\text{max}} = 500$ nm, \bullet), and a benzene slurry of DT@NaY (1.0 mg mL⁻¹, $\lambda_{\text{max}} = 490$ nm, \blacksquare).

CP/MAS ¹³C solid state NMR of the zeolite sample revealed only a weak and very broad signal in the aromatic region, as one would expect from a paramagnetic species. The fluorescence emission spectra of DT@NaY and DT in benzene were measured and compared (Figure 2). Upon 330-nm excitation, both the samples showed a fluorescence emission in the same spectral region: DT in benzene (1×10^{-4} M) had a fluorescence maximum at 470 nm, DT@NaY showed a maximum at 500 nm in the solid state and at 490 nm in a 1 mg mL⁻¹ benzene slurry. It is possible that the 30 nm shift in the fluorescence maxima is a result of in-cavity electrostatic interactions experienced by the probe. Accordingly, the presence of benzene in the cavity (when the solid is in a slurry) shifts the maximum toward the solution value. Neither dansyl chloride nor 4-amino TEMPO are fluorescent.

The spectral data clearly support the conclusion that DT was successfully prepared inside the cavities of NaY by ship-in-a-bottle-synthesis. On the basis of recovered materials and by means of an elemental analysis the occupancy number of DT@NaY was calculated to be $\langle S \rangle = 0.1$ (with an intrinsic reaction yield of ca. 20%). To the best of our knowledge this is the first reported example of base-catalyzed ship-in-a-bottle synthesis.

Applications of DT@NaY. As mentioned in the Introduction, the aim of the present study was to monitor radical diffusion processes within NaY zeolite pores. We initially endeavored to prove that the supramolecular composite DT@NaY is an effective sensor, able to trap carbon-centered radicals when they are present within NaY cavities. With this idea in mind, 2,2'-azobisisobutyronitrile (AIBN) was co-included in the zeolite material and its thermal decomposition at 70 °C

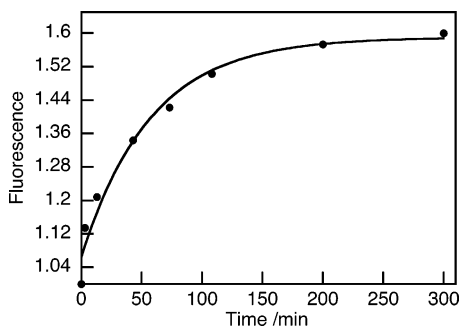


Figure 3. Fluorescence growth (normalized to 1.0 at time = 0) measured after heating (70 °C) a solid sample of DT@NaY with co-included AIBN (AIBN $\langle S \rangle = 0.5$, $\lambda_{\text{ex}} = 305$ nm, $\lambda_{\text{em}} = 550$ nm).

in a solid DT@NaY sample was examined by monitoring the time evolution of the fluorescence emission (AIBN inclusion was performed by stirring DT@NaY in a hexane solution of AIBN at room temperature until an occupancy of $\langle S \rangle = 0.5$ was reached, see Experimental Section for details).

Figure 3 shows the time dependence of the normalized fluorescence growth ($\lambda_{\text{ex}} = 305$ nm, $\lambda_{\text{em}} = 550$ nm, measured after cooling the sample to room temperature). In accordance with previously reported results^{7–17} the fluorescence growth reaches a plateau (in this case after ca. 120 min) indicating the end of the coupling between the nitroxyl moiety of the probe and carbon-centered radicals. The half-life of AIBN in solution is ~ 5 h.²⁷ Notably, the final fluorescence intensity is within the range previously observed for measurements of DT in solution when monitoring at 550 nm.²⁰ The energy-transfer fluorescence quenching by the nitroxide moiety, and therefore the quantum yield of the paramagnetic species, should be largely insensitive to zeolite encapsulation. It would not be unusual, however, for the diamagnetic species to experience an enhancement in fluorescence due to the suppression of nonradiative modes. A reference sample of DT@NaY containing no AIBN did not show any fluorescence increase when heated under the same conditions (data not shown).

Having demonstrated the ability of DT@NaY to trap radicals that have been generated within the zeolite we proceeded to investigate the behavior of radicals generated outside of the zeolite supercages and their subsequent percolation through the microarray. To accomplish this we monitored the fluorescence evolution of a slurry composed of 1.0 mg mL⁻¹ of DT@NaY in a hexane solution of 3,3'-diphenyl-3H,3H-[3,3']bibenzofuranyl-2,2'-dione, **7**, which was chosen as the radical precursor. The ability of **7** to yield 3-phenyl-2-coumaranone radicals, **8**, (Scheme 4) via homolytic C–C bond cleavage upon heating and the fate of the resulting radicals is well documented in the literature.²⁸ Depending on the nature of the solvent and the temperature, the favored process is either recombination to form the starting dimer,²⁹ coupling affording head-to-tail dimers and tetramers,³⁰ or hydrogen atom abstraction from a donor medium to yield 3-phenyl-2-coumaranone **9**.²⁹

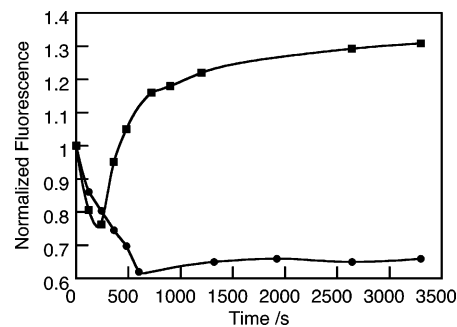
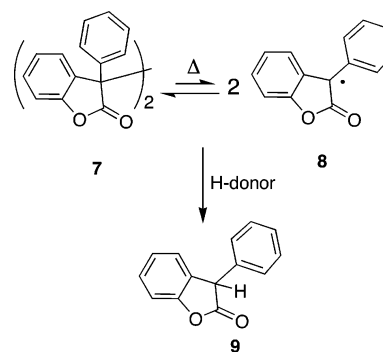


Figure 4. Fluorescence evolution for a benzene slurry of 1 mg mL⁻¹ DT@NaY in the absence (●) and presence (■, 1.0 mg mL⁻¹) of the radical precursor ($\lambda_{\text{ex}} = 330$ nm, $\lambda_{\text{em}} = 550$ nm).

Scheme 4. Reactivity of 3,3'-Diphenyl-3H,3H-[3,3']bibenzofuranyl-2,2'-dione, **7**



Compound **7**, effectively the dimer of radical **8**, was particularly suitable for the present study because only the 3-phenyl-2-coumaranone radicals are small enough to diffuse through the NaY windows, whereas the direct inclusion of the dimer is prevented by its dimensions; thus radicals are formed exclusively in the solution. Furthermore, the persistency of 3-phenyl-2-coumaranone radicals³¹ ensures that they will live long enough to migrate through the pores. A fluorescence increase over time should then be observed as radicals penetrate the pores, and encounter and couple with the embedded prefluorescent probe. The resulting product is bulky but should be comfortably shared between two supercages.

Samples were prepared at room temperature and heated to 50 °C. The fluorescence emission was recorded both during the temperature increase and after reaching 50 °C. Figure 4 shows the fluorescence evolution measured upon heating a hexane slurry of DT@NaY under N₂ ($\lambda_{\text{ex}} = 330$ nm, $\lambda_{\text{em}} = 550$ nm). In the absence of dimer **7** (●) a fluorescence decrease reaching a plateau after 600 s was observed; this is the time required by the sample, initially at room temperature, to reach a temperature of 50 °C (i.e., the DT@NaY fluorescence quantum yield decreases as a result of the temperature increase). When the radical precursor was present in the slurry (1.0 mg mL⁻¹, ■) the initial emission decrease lasted only 300 s, during which time radicals were formed in the solution, diffused into the pores, and subsequently encountered and coupled with embedded probe molecules. After this initial decrease, which was

(27) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: New York, 1995.

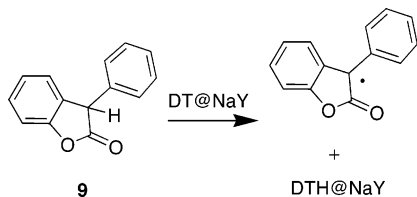
(28) Karafiloglou, P.; Catteau, L. P.; Lablanche-Combiere, A.; Ofenberg, H. *J. Chem. Soc., Perkin Trans.* **1977**, *2*, 1545–1548.

(29) Lohray, B. B.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Am. Chem. Soc.* **1984**, *106*, 7352–7359.

(30) Catteau, J. P.; Karafiloglou, P.; Lablanche-Combiere, A. *J. Chem. Res. Synop.* **1980**, 3901–3910.

(31) Bejan, E. V.; Font-Sanchis, E.; Scaiano, J. C. *Org. Lett.* **2001**, *3*, 4059–4062.

Scheme 5. Intercavity Reaction between 3-Phenyl-2-coumaranone and DT



common to both samples, a fluorescence growth reaching an approximate plateau around 1500 s was observed for the dimer-containing slurry. Continued measurements were not practical because of the elevated temperature and the small solvent volume. The observed time evolution is direct proof that, at these temperatures and with this concentration of the dimeric precursor, radical penetration into NaY pores from the solution takes place within minutes. Notably, no DT was recovered in the solution (tested by TLC and HPLC analysis) at the end of either experiment. The rate-determining step for the overall process cannot be unequivocally identified from these experiments; possible candidates are the initial penetration into the zeolite particle (i.e., a surface process), diffusion within the zeolite, or (less likely) the actual reaction between the carbon radical and the nitroxide. The elevated temperature may also cause an increase in both the rate of percolation and the rate of the inherently fast radical recombination reaction.

As a final demonstration of the utility of matrix-immobilized prefluorescent probes we undertook preliminary investigations of hydrogen atom transfer in microheterogeneous environments. As mentioned in the Introduction, the ability of prefluorescent probes to abstract hydrogen atoms from good donors such as antioxidants (synthetic polymer stabilizers,³² polyphenols,^{33,34} and vitamin C²⁰) has been reported in the literature and is currently under investigation. By monitoring the fluorescence increase resulting from hydroxylamine formation in the presence of an excess of the antioxidant in question (pseudo-first-order conditions) the rate constants of hydrogen atom transfer (k_{HT}) have been calculated for a number of compounds. For example, Likhtenstein et al. measured a value of $k_{HT} = 7 \text{ M}^{-1} \text{ s}^{-1}$ for vitamin C in fruit juices (Scheme 2).²⁰

In the present study, hydrogen transfer from 3-phenyl-2-coumaranone, a synthetic antioxidant, was investigated using DT@NaY to observe the behavior of the antioxidant as it diffuses through the zeolite pores, encounters the prefluorescent probe, and consequently forms carbon-centered radicals and fluorescent DTH within the cavities (Scheme 5). In a related example, the use of prefluorescent probes to determine H-abstraction rate constants for synthetic antioxidants has been recently reported for a variety of phenolic antioxidants.³³

Figure 5 shows the fluorescence increase ($\lambda_{ex} = 330 \text{ nm}$, $\lambda_{em} = 550 \text{ nm}$) from a slurry containing 1.0 mg mL^{-1}

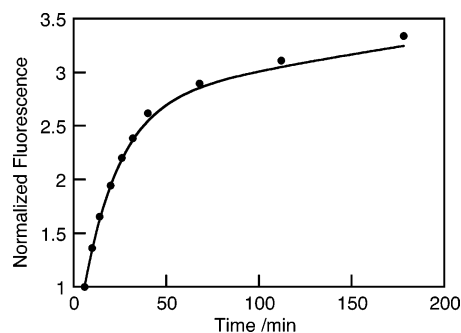


Figure 5. Fluorescence evolution ($\lambda_{ex} = 330 \text{ nm}$, $\lambda_{em} = 550 \text{ nm}$) of a slurry containing 1.0 mg mL^{-1} DT@NaY in a solution of 3-phenyl-2-coumaranone (0.01 M) in N_2 -purged benzene.

of DT@NaY in a solution of 3-phenyl-2-coumaranone (0.01 M) in N_2 -purged benzene at room temperature. As before, no DT is recovered from the solution indicating that there is no leaching of the entrapped species. In this case, the emission continues to increase exponentially until reaching a plateau after $\sim 100 \text{ min}$. As in the previous example, the rate-determining step in this process is unlikely to be the hydrogen abstraction step and may be related to the percolation of the molecule through the pores prior to encountering a nitroxide. In this experiment 3-phenyl-2-coumaranone is present in large excess, so the most likely fate of the carbon-centered radicals generated by hydrogen abstraction is reaction with another molecule of the relatively ubiquitous 3-phenyl-2-coumaranone, effectively leading to radical center migration. Considering the experiment is conducted at room temperature, the observed plateau in the fluorescence increase may indicate that all of the DT has been consumed or it may indicate a "molecular gridlock" where unreacted DT is present but is no longer easily accessible to the percolating coumaranone molecules or radicals. We would expect the congestion to be more pronounced in this case due to the higher concentration of coumaranone and the ambient temperature, which shifts the dimer-radical equilibrium toward coupling products. The gentle slope toward the end of the reaction may indicate that some reaction continues slowly at this point.

In conclusion, we report the first example of a base-catalyzed ship-in-a-bottle synthesis for the immobilization of a prefluorescent probe in the cavities of faujasite NaY to yield the supramolecular assembly DT@NaY. This material was successfully employed both in the solid state to study the intercavity diffusion of carbon-centered radicals produced by AIBN thermolysis and in a slurry to study the penetration and diffusion of carbon-centered radicals generated in solution. Additionally, DT@NaY was shown to be reactive toward hydrogen atom abstraction from 3-phenyl-2-coumaranone, a synthetic antioxidant.

Experimental Details

Dansyl chloride, 4-amino-TEMPO, and AIBN were purchased from Aldrich and used without further purification. Pyridine was purchased from Aldrich and dried on molecular sieves before use. 3,3'-diphenyl-3H,3H'-[3,3']bibenzofuran-2,2'-dione and 3-phenyl-2-coumaranone³⁵ were synthesized following the procedures reported in the literature. Analytical grade solvents were used.

(32) Aspee, A.; Aliaga, C.; Ricci, A.; Scaiano, J. C. unpublished results.

(33) Aliaga, C.; Aspee, A.; Scaiano, J. C. *Org. Lett.* **2003**, *5*, 4145–4148.

(34) Aliaga, C.; Lissi, E. A.; Augusto, O.; Linares, E. *Free Radical Res.* **2003**, *34*, 659–665.

Ground-state diffuse reflectance spectra were measured on a Cary 1E spectrophotometer equipped with a diffuse reflectance attachment and using Spectralon as a standard. Fluorescence measurements were recorded on a PTI fluorimeter using a front-face geometry for both solid and slurry samples. TLC analyses were performed on silica gel 60 F₂₅₄ plates purchased from Merck (hexane/ethyl acetate mixtures as the eluant). CP/MAS ¹³C NMR spectra were measured on a Bruker AVANCE 500 spectrometer with a 5-kHz spin rate.

DT@NaY Base-Catalyzed Synthesis. A 1-g portion of NaY was calcined overnight at 480 °C and then added to 15 mL of hexane; the slurry was degassed with nitrogen. Pyridine (50 μL) was added to the hexane slurry at room temperature and stirred overnight. 4-Amino TEMPO (50.2 mg) was then added, and the entire mixture was stirred for a further 24 h, after which a TLC analysis showed no presence of 4-amino TEMPO in the solvent. Dansyl chloride (80 mg) was then added and the slurry was stirred for three more days. After this time, the solid was collected by filtration and washed 5× with 5 mL of hexane. A mixture of dansyl chloride, pyridine, 4-amino TEMPO, and dansyl-TEMPO (90 mg overall) was recovered. The zeolite sample was then extracted with a Soxhlet solid-liquid extractor for 3 days. After 1 day, traces of dansyl-TEMPO were found in the extraction solvent (3 mg), after the second and third day nothing further was recovered.

Thermal Decomposition of AIBN in DT@NaY. To 0.5 g of DT@NaY in 10 mL of hexane, 49 mg of AIBN was added and the suspension was stirred overnight at room temperature, filtered, and washed 5× with 5 mL of hexane. UV analysis of the recovered washing solution indicated complete inclusion

of AIBN ($\langle S \rangle = 0.5$). The solid sample was then dried under nitrogen to completely remove the solvent and was heated at 70 °C in a sandbath. Before measuring the fluorescence intensity the sample was cooled in a waterbath for 10 min to allow equilibration at room temperature ($\lambda_{\text{ex}} = 305$ nm, $\lambda_{\text{em}} = 550$ nm).

Diffusion of 3-Phenyl-2-coumaranone Radicals Through the Pores of DT@NaY. A 2-mL aliquot of 3,3'-diphenyl-3*H*,3'*H*-[3,3']bibenzofuranyl-2,2'-dione in hexane (1.2×10^{-3} M) was placed in a fluorescence cuvette and 2 mg of DT@NaY was added (1.0 mg mL⁻¹). The slurry was purged with nitrogen and stirred for 10 min at room temperature. The cuvette was then placed in the fluorimeter chamber and heated to 50 °C while stirring. The fluorescence intensity was measured every 30 min ($\lambda_{\text{ex}} = 330$ nm, $\lambda_{\text{em}} = 550$ nm).

Hydrogen Atom Transfer Reaction Between 3-Phenyl-2-coumaranone and DT@NaY. A 2-mL aliquot of 3-phenyl-2-coumaranone in benzene (0.01 M) were placed in a fluorescence cuvette and 2 mg of DT@NaY was added (1.0 mg mL⁻¹). The slurry was purged with nitrogen and stirred for 5 min at room temperature. The fluorescence evolution was monitored at room temperature under stirring ($\lambda_{\text{ex}} = 330$ nm, $\lambda_{\text{em}} = 550$ nm).

Acknowledgment. Thanks to the Natural Sciences and Engineering Council of Canada for generous support in the form of a discovery grant (J.C.S.) and a PGS-B scholarship (M.N.C.). We also thank Glenn Facey for assistance with CP/MAS NMR.

CM0499343

(35) Pawda, A.; Dehm, D.; Oine, T.; Lee, G. *J. Am. Chem. Soc.* **1975**, *97*, 1837–1842.