Zeolites as Templates for Preparation of Large-Ring Compounds: Intramolecular Photocycloaddition of Diaryl Compounds

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Abstract: The fluorescence spectra and photocycloadditions of poly(ethylene glycol) labeled at the chain terminal with 2-naphthyl groups (N−P$_n$−N) or one 9-anthryl and one 1-naphthyl groups (N−P$_n$−A) and polymethylene end-labeled with two 2-naphthyl groups (N−M_n−N) or two 9-anthryl groups (A−M_n−A) included in NaY zeolite have been investigated. At loading levels less than 1 guest molecule per 10 supercages of zeolite, N−P$_n$−N, N−M_n−N, and A−M_n−A exclusively exhibit intramolecular excimer emission. Selective excitation of the naphthyl moiety in N−P$_n$−A mainly results in emission from the anthryl chromophore and intramolecular exciplex fluorescence. Irradiation of the above compounds leads to formation of intramolecular photocyclomers to the exclusion of intermolecular products. These results are explained in terms of the compartmentalization of the guest molecules in the supercages of NaY zeolite. Thus, this work demonstrates the utility of micropores of zeolites to promote the formation of large-ring compounds in synthetically useful quantities. Of particular interest is the enhanced formation of the cross-photocyclomers of anthracene and naphthalene derivatives (a process not observed in homogeneous solution) in high yields.

Introduction

The construction of macrocyclic compounds continues to be an important topic of synthetic organic chemistry.[1] A bifunctional molecule may undergo either intramolecular or intermolecular reactions. Intramolecular reaction gives macrocyclic ring-closure products, while intermolecular reaction results in dimers, oligomers, and polymers. Thus, the cyclization reaction suffers from the competition of the polymerization reaction. The rates of the latter are dependent on the concentration of the substrate, while those of the former are not, since the effective concentration for the reaction is kept constant by the function of a molecular chain linking the two functional groups. Hence, high substrate concentrations favor polymerization while cyclization proceeds in good chemical yields only at low concentrations.[2] Ziegler was the first to apply this principle to the synthesis of large-ring compounds by a high dilution method.[3] In general, the syntheses of many-membered rings are performed at substrate concentrations as low as 1×10^{-5} M. This corresponds in a batch reaction to $\mathbf{1} \times 10^5$ L of solvent for each mole of substrate! To synthesize large-ring compounds at high substrate concentrations, proper choice of solvents and using hydrophobic or lipohobic interactions to induce the flexible linking chains to self-coil, thus increasing the probability of the end-to-end encounters, has proved to be effecitve.[1i,4−6] Jiang and co-workers[1i] studied the intramolecular photochemical cycloaddition of 1,10-dicinnamoxydecane in aqueous organic binary mixed solvents and obtained 16-membered macrocyclic products with 90% yield. Nishimura et al.[4] photochemically synthesized 29-membered macrorings in high yield using 0.1 M methanol or acetonitrile solutions. Desvergne et al.[5] obtained a 21-membered ring from poly(ethylene glycol) labeled at the chain terminal with 9-anthryls in benzene. Tung and co-workers[6] photochemically synthesized a series of large-ring compounds form naphthyl-labeled poly(ethylene glycol) oligomers in nonpolar solvents, and from aryl-labeled polymethylene in aqueous organic binary mixed solvents.

Here, we report a new approach to synthesize large-ring compounds in high yields under high substrate concentrations. Our approach involves microporous solids as templates and hosts for the cyclization reactions. The size of the micropore has been chosen to permit only one substrate molecule to fit within each. Thus, intermolecular reactions are hindered and cyclization can occur without competition under conditions of high loading. We find that Y-type zeolites can be used as such microvessels for intramolecular photocycloadditions of diaryl compounds with long flexible chains.

Zeolites may be regarded as open structures of silica in which silicon has been substituted by aluminum in a well-defined fraction of the tetrahedral sites.[7] The frameworks thus obtained contain pores, channels, and cages of different dimensions and shapes. The structure of Y-type zeolite consists of an interconnecting three-dimensional network of relatively large spherical

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[1] (a) Evans, P. A.; Holmers, A. B. *Tetrahedron* **1991**, *47*, 9131. (b) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95. (c) Griesbeck, A. G.; Henz, A.; Hirt, J. *Synthesis* **1996**, *11*, 1261. (d) Mandolini, L. In *Advanced Physical Organic Chemistry*; Gold, V., Bethell, D., Ed.; Academic Press: London, 1986; vol. 22, pp 1−112, and references therein. (e) Lehn, J. M. *Supramolecular Chemistry*, VCH: Weinheim, 1995. (f) Vögtle, F., Ed. *Topics Curr. Chem.* **1983**, 113. (g) Weber, E.; Vogtle, F., Eds. *Topics Curr. Chem.* **1991**, 161. (h) Proter, N. W. *J. Am. Chem. Soc.* **1986**, *108*, 2787. (i) Jiang, X. K.; Hui Y. Z.; Fei, Z. X. *J. Chem. Soc., Chem. Commun.*, **1988**, 689.

[2] Ruggli, P., *Liebigs Ann. Chem.* **1912**, *392*, 92; **1913**, *399*, 174; **1916**, *12*, 1.

[3] Ziegler, K. In *Methoden der Organischen Chemie* (Houben-weyl); Muller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1955; Vol. 4/2.

[4] Inokuma, S.; Sakai, S.; Nishimura, J. *Topics Curr. Chem.* **1994**, *172*, 87.

[5] Desvergne, J. P.; Bouas-Laurent, H. *Isr. J. Chem.* **1979**, *18*, 220.

[6] (a) Tung, C. H.; Li, Y.; Yang, Z. Q. *J. Chem. Soc., Faraday Trans.* **1994**, *90(7)*, 947. (b) Tung, C. H.; Wang, Y. M. *J. Am. Chem. Soc.* **1990**, *112*, 6322. (c) Tung, C. H.; Xu, C. B. In *Photochemistry and Photophysics*; CRC Press: Boca Raton, 1991; Vol. 4, Chapter 3, p 177.

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cavities (supercages) with a diameter of about 13 Å.[8] Each supercage is connected tetrahedrally to four other supercages through 7.4-Å diameter windows or pores. As an indication of their volume, each supercage can include five molecules of benzene, two molecules of naphthalene, or two molecules of pyrene.[9] Thus, one might expect that both aryl parts of a molecule with α,ω-diaryl groups separated by a flexible chain can be included in one supercage, and the intramolecular reactions between the two aryl groups should be enhanced. On the other hand, according to a Poisson distribution, as long as the loading level is less than one guest molecule per 10 supercages, there is less than a 5% probability to find two substrate molecules in one supercage, and the intermolecular reactions should be inhibited.[10] The unit cell composition of NaY zeolite crystal is $Na_{53}[(AlO_2)_{53}(SiO_2)_{139}]\cdot 250H_2O$, and it is cubic with a dimension of ca. 25 Å.[7a,11] Thus, a typical particle of 1 μm diameter contains thousands of interconnected supercages, and the concentration of the supercages is ca. 500 μmol/g of zeolite.[11,12] Assuming that a loading level of one substrate molecule per 10 supercages completely inhibits intermolecular reaction (vide infra) while cyclization still proceeds, only **2** $\times 10^4$ g of zeolite are needed for each mole of substrate! This corresponds to 40 g of NaY zeolite for each gram of substrate whose molecular weight is 500. This amount of zeolite is more than 10^3 times smaller compared with that of the solvent in solution-phase reactions that allow cyclization to dominate.

Although the photochemical behavior of organic compounds adsorbed on zeolites has been extensively studied,[13] the use of zeolites as microreactors to enhance the formation of large-ring compounds has not been reported.[14] In the present work, we investigate the intramolecular photocycloadditions of diaryl compounds in Scheme 1 upon their inclusion in supercages of NaY zeolites. As expected from the analysis above, at loading levels less than 1 molecule of a diaryl compound per 10 supercages of NaY zeolite only intramolecular photocycloaddition is observed.

Scheme 1

$Np\text{-}COO\text{-}(CH_2CH_2O)_n\text{-}CO\text{-}Np$

$N\text{-}P_n\text{-}N$ (n = 4, 5, 10, 12) (Np = 2-naphthyl)

$Np\text{-}COO\text{-}(CH_2)_n\text{-}OCO\text{-}Np$

$N\text{-}M_n\text{-}N$ (n = 3, 5, 8, 10) (Np = 2-naphthyl)

$An\text{-}CH_2OCO(CH_2)_{n\text{-}2}\text{-}COOCH_2\text{-}An$

$A\text{-}M_n\text{-}A$ (n = 6, 10) (An= 9-anthryl)

$NpCOO\text{-}(CH_2CH_2O)_n\text{-}COCH_2CH_2\text{-}An$

$N\text{-}P_n\text{-}A$ (n = 3, 4, 5) (An = 9-anthyl, Np = 1-naphthyl)

Results and Discussion

Photocycloaddition of N−P_n−N and N−M_n−N. Irradiation of alkyl 2-naphthoates is known to yield a "cubane-like" photocyclomer as the unique product (Scheme 2), although six isomeric cyclomers are formally possible.[6,15] This selectivity originates from two restrictions. First, the photocycloaddition occurs only between the substituted rings. Second, in the cyclomer the substituents are in a head-to-tail orientation. We have previously demonstrated that the yield of this photocyclomer is dependent on the square of the light intensity, suggesting that the formation of the cubane-like photocyclomer for alkyl 2-naphthoates is a two-photon process.[6a] Irradiation of N−P_n−N in organic solutions, such as acetonitrile, can lead either to intra- or intermolecular cycloadditions. At concentrations higher than 10^{-3} M, the main product is the intermolecular photocyclomer.

By contrast, irradiation of N−P_n−N adsorbed on NaY zeolite results in an intramolecular photocyclomer. Inclusion of the diaryl compounds within activated NaY zeolite was achieved using cyclohexane as the solvent. The zeolite with adsorbed substrate was isolated by filtration and dried under reduced pressure. The loading level was kept at ca. 50 μmol of substrate per gram of zeolite (ca. 1 molecule per 10 supercages). This material was then transferred to a quartz vessel. After evacuation, the vessel was sealed, and the sample was irradiated with light $\lambda > 280$ nm in order to protect the photocyclomers from decomposition. The photocycloaddition was followed by fluorescence spectra. Figure 1 shows the fluorescence spectra of N−P_4−N, which is typical of the studied N−P_n−N, as a function of irradiation time. This compound included within NaY exclusively exhibits excimer fluorescence (see below). As the irradiation is prolonged, the fluorescence intensity is decreased, although the general feature of the spectrum remains unchanged. Generally, after 4 h of irradiation, the conversion was near 100%. Similar conversions were obtained in acetonitrile after about 1 h irradiation.

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(7) For background information on zeolites: (a) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; John Wiley and Sons: New York, 1974. (b) Dyer, A. *An Introduction to Zeolite Molecular Sieves*; John Wiley and Sons: New York, 1988. (c) Van Bekkum, H.; Flanigen, E. M.; Jansen, J. C. *Introduction to Zeolite Science and Practice*; Elsevier: Amsterdam, 1991.

(8) (a) Jacobs, P. A.; Beyer, H. K.; Valyon, J. *Zeolites* **1981**, *1*, 161. (b) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Structure Commission of IZA; Polycrystal Book Service: Pittsburgh, 1978. (c) Smith, V. J. In *Zeolite Chemistry and Catalysis*; ACS Monograph 171; Rabo, J. A., Ed.; American Chemical Society: Washington, DC, 1976.

(9) (a) Suib, S. L. In *Photochemistry and Photophysics,* Rabek, J., Ed.; CRC: Boca-Raton, 1991; Vol. 3. (b) Liu, X.; Iu, K. K.; Thomas, J. K. *J. Phys. Chem.* **1989**, *93*, 4120. (c) Iu, K. K.; Liu X.; Thomas J. K. *Mater. Res. Soc.* **1991**, *223*, 119. (d) Dinesenko, G. I.; Lisovenko, V. A. *Zl. Prikl Spektrosk.* **1971**, *14*, 702. (e) Incavo, J. A.; Dutta, P. K. *J. Phys. Chem.* **1990**, *94*, 3075. (f) Baretz, B. H.; Turro, N. J. *J. Photochem.* **1984**, *24*, 201.

(10) Assuming that the substrate molecules are randomly distributed over the supercages of the zeolite, the distribution can be expressed by Poisson equation. $P(n) = \lambda^n \exp(-\lambda)/n!$ where λ is the molar ratio of the substrate molecules to the supercages, and $P(n)$ the probability of n substrate molecules in a supercage. At the loading of 50 μmol g^{-1} ($\lambda = 0.1$) $P(1)$ and $P(2)$ were calculated to be 0.09 and 4.5×10^{-3} respectively. Thus, the probability to find one N−P_n−N molecule in one supercage is 20 times of that to find 2 N−P_n−N molecules in one supercage. This suggests that the amount of the intermolecular photodimer is less than 5% in the photochemical products. We noticed that the above equation assumes a random distribution of the substrate molecules in the supercages of the zeolite. The molecular size of the substrates used in this work are large, and no more than two molecules can fit inside one supercage. Thus, the applicability of the above equation is limited.

(11) Borja, M.; Dutta, P. K. *Nature* **1993**, *362*, 43.

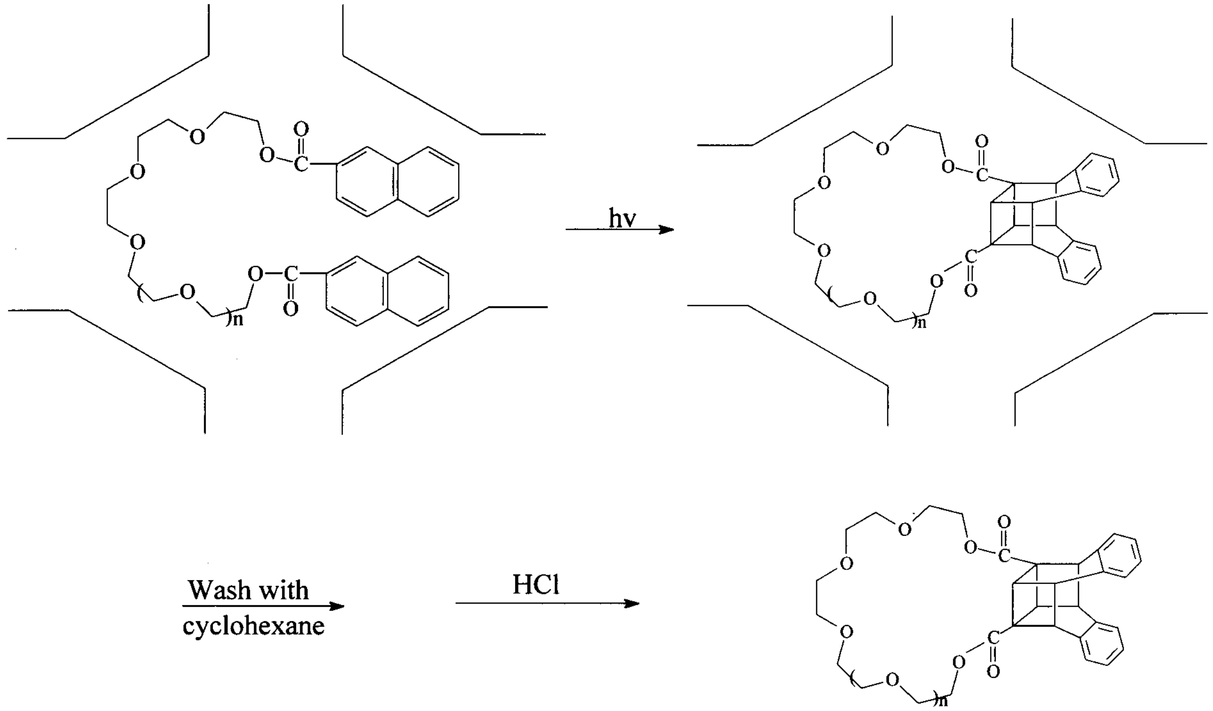
(12) (a) Laine, P.; Lanz, M.; Calzaferri, G. *Inorg. Chem.* **1996**, *35*, 3514. (b) Dutta, P. K.; Turbeville, W. *J. Phys. Chem.* **1992**, *96*, 9410. (c) Kim, Y.; Mallouk, T. E. *J. Phys. Chem.* **1992**, *96*, 2879.

(13) For a review of the photochemistry of organic molecules adsorbed on zeolites, see (a) Turro, N. J. *Pure Appl. Chem.* **1986**, *58*, 1219. (b) Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, *26*, 530. (c) Ramamurthy, V., Weiss, R. G.; Hammond, G. S. *Adv. Photochem.* **1993**, *18*, 69. (d) Ramamurthy, V.; Turro, N. J. *J. Inclus. Phenom. Mol. Recogn. Chem.* **1995**, *21*, 239. (e) Alvaro, M.; Garcia, H.; Garcia, S.; Marquez, F.; Scaiano, J. C. *J. Phys. Chem. B.*, **1997**, *101*, 3043 and previous papers in this series.

(14) Lei, X.-G.; Doubleday, C. E., Jr.; Zimmt, M. B.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 2444.

(15) (a) Collin, P. J.; Roberts, D. B.; Sugowdz, G.; Wells, D.; Sasse, W. H. F. *Tetrahedron Lett.* **1972**, 321. (b) Kowala, C.; Sugowdz, G.; Sasse, W. H. F.; Wunderlich, J. A. *Tetradron Lett.* **1972**, 4721. (c) Teitei, T.; Wells, D.; Sasse, W. H. F., *Aust. J. Chem.* **1976**, *29*, 1783.

Scheme 2



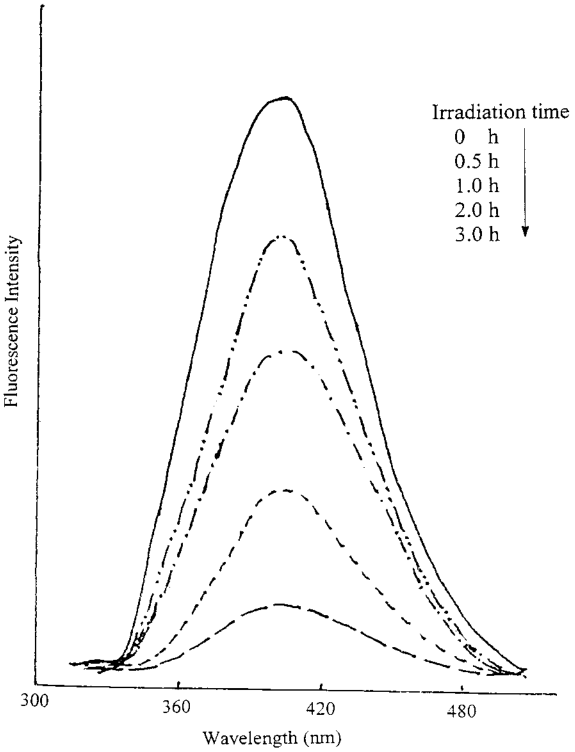


Figure 1. Fluorescence spectra of N−P$_4$−N included in NaY zeolite as a function of irradiation time; loading level: 50 μmol g^{-1}; λ_{ex} = 280 nm.

Once formed, the photocyclomer is trapped inside the supercage of the zeolite, since the 7.4-Å window is too narrow to allow it to escape.[16] We used PCModel 6.00 program to calculate the energies of the various conformations of the photocyclomer and found that the cyclomer of N−P$_4$−N in its lowest energy conformation has a size of ca. 6.6 Å × 8.2 Å × 12.5 Å, suggesting that this molecule has difficulty escaping through the zeolite window, but still can be accommodated in the supercage. However, the aluminosilicate framework of Y zeolite can be dissolved in strongly acidic media so that the photocyclomer is released into solution and can be subsequently isolated.[14,17] Thus, we first extracted the unreacted starting material with dichloromethane and then isolated the product by dissolving the zeolite framework in concentrated HCl followed by extraction with ether. Generally, the products were obtained in high purity by this procedure. *Only the intramolecular ring-closure photocyclomers were obtained and no intermolecular products were detected by HPLC.* The yields of the intramolecular products were close to 100% based on the consumption of the starting material. In Table 1 are given the conversion and mass balance for all the photocycloadditions of N−P$_n$−N. The assignment of the intramolecular reaction relies on the observation that the *m*/*z* values of the molecular ions of the products in the mass spectra are identical to those of the corresponding starting materials. Furthermore, in the ^{1}H NMR spectra of the products, no protons assignable to the naphthyl group were detected. The structure proposed for the cubane-like photocyclomer rests mainly on its ^{1}H NMR spectrum, which is very similar to that reported.[6,15] The spectral details and assignments for the intramolecular photocyclomer of N−P$_5$−N are given in Table 2. They are typical of the N−P$_n$−N studied in the present work.

The effect of the loading level of N−P$_n$−N in NaY zeolite on the photocycloaddition was examined. Between 50 and 5 μmol g^{-1} (~40 mg and ~4 mg of N−P$_{10}$−N per gram of zeolite) intramolecular photocyclomers were the only products detected. At higher loading levels, increasing amounts of intermolecular photocyclomers were also obtained. The exclusive formation of intramolecular photocyclomers at loading

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[16] The existence of the photodimers in the supercages was also evidenced by the following observation. After photolysis and washing with dichloromethane until all starting material was extracted, the sample was reirradiated at λ < 280 nm, where the dimer reverts to starting material, N−P$_n$−N. The regenerated starting material could be extracted easily by dichloromethane.

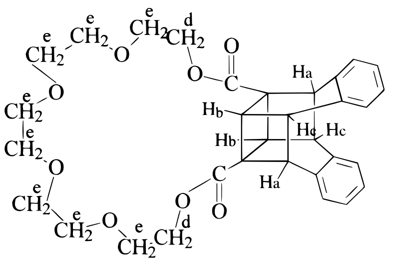
[17] Maruszewski, K.; Strommen, D. P.; Handrich, K.; Kincaid, J. R. *Inorg. Chem.* **1991**, *30*, 4579.

Table 1. Conversion, Mass Balance and Selectivity in the Photocycloaddition of Diaryl Compounds Included in NaY Zeolite

substrate	irradiation time (h)	conversion (%)	mass balance (%)	selectivity
$N-P_4-N$	4	100	>95	intramolecular cyclomer h−t
$N-P_5-N$	4	100	>95	intramolecular cyclomer h−t
$N-P_{10}-N$	4	100	>95	intramolecular cyclomer h−t
$N-P_{12}-N$	4	100	>95	intramolecular cyclomer h−t
$N-M_3-N$	4	100	>95	intramolecular cyclomer h−t
$N-M_5-N$	4	100	>95	intramolecular cyclomer h−t
$N-M_8-N$	4	100	>95	intramolecular cyclomer h−t
$N-M_{10}-N$	4	100	>95	intramolecular cyclomer h−t
$A-M_6-A$	2	60[a]	>95	intramolecular cyclomer, h−h
$A-M_{10}-A$	2	>80[a]	>95	intramolecular cyclomer h−t/h−h = 4
$A-P_3-N$	4	>80	>90	intramolecular cyclomer h−t
$A-P_4-N$	4	>80	>90	intramolecular cyclomer h−t
$A-P_5-N$	4	>80	>90	intramolecular cyclomer h−t

[a] The conversion was calculated based on the yield of the isolated products.

Table 2. ^{1}H NMR Data and Assignments of the Cyclomers of $N-P_5-N$



N-P$_5$-N

δ (ppm)	split	I	H
6.95−7.00	m	8H	Ar
4.52	d	2H	H_a
4.39	dd	2H	H_c
4.25	m	4H	H_d
3.86	d	2H	H_b
3.6−3.8	m	16H	H_e

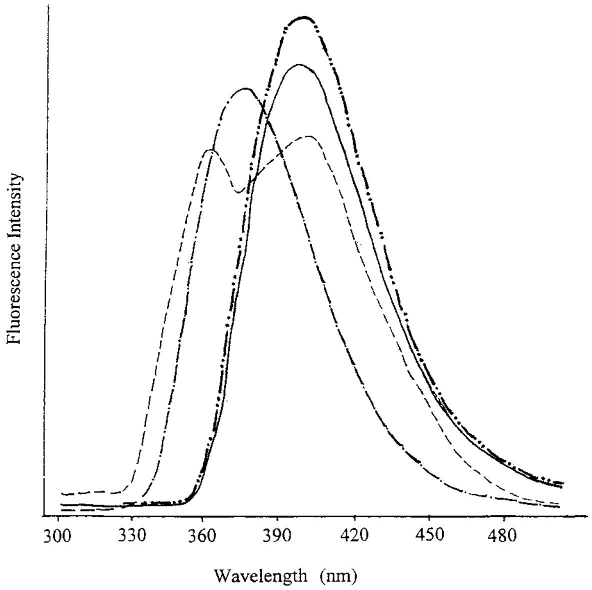


Figure 2. Fluorescence spectra of $N-P_4-N$ in methanol (1×10^{-4} M - - -) and included in NaY zeolite (10 μmol g^{-1}—; 50 μmol g^{-1} -••-). The fluorescence spectrum of $N-P_4$ in NaY zeolite is also given (20 μmol g^{-1} -•-•-). λ_{ex} = 280 nm.

levels $\leq$50 μmol g^{-1} is attributed to the separation of the substrate molecules from each other by the supercages of the zeolite while the terminal aryl groups of one $N-P_n-N$ molecule can be compartmentalized in one supercage. In such a case, there is inadequate space in the supercage to include an aryl group of another molecule. Thus, these included $N-P_n-N$ molecules will undergo intramolecular photocycloaddition exclusively. Additionally, since the loading level is less than one molecule per 10 supercages, it is unlikely that an occupied supercage will have a neighbor with another $N-P_n-N$ molecule. Thus, intermolecular photocycloaddition is excluded.

To obtain further information on the compartment experienced by the two terminal groups of a $N-P_n-N$ molecule in a supercage, their fluorescence spectra were examined. Figure 2 shows the fluorescence spectra of $N-P_4-N$ included in NaY zeolite and in methanol solution. The fluorescence spectrum of the monochromophoric compound N_p-COO(CH$_2$CH$_2$O)$_4$-COCH$_3$ ($N-P_4$, N_p = 2-naphthyl) in NaY zeolite is also given in Figure 2. In methanol solution at concentrations below 1×10^{-4} M $N-P_4-N$ shows both the monomer (λ_{max} = 360 nm) and excimer (λ_{max} = 400 nm) emission. At such concentrations the ratio of the fluorescence intensities of excimer to monomer is independent of concentration, suggesting that the excimer is intramolecular. This ratio is dependent on the length of the linking chain of $N-P_n-N$, with a short chain favoring excimer formation. The fluorescence of $N-P_n-N$ differed significantly when included in NaY zeolite compared to those in methanol solution. At the loading levels below 50 μmol g^{-1}, while the model compound $N-P_4$ only gives monomer emission (λ_{max} = 370 nm), $N-P_4-N$ exclusively exhibits excimer fluorescence centered at 400 nm. At the loading level as low as 1 μmol g^{-1}, only excimer emission was observed, suggesting that the excimer is intramolecular. The excitation spectra of the fluorescence for $N-P_4-N$ and $N-P_4$ included in NaY zeolite were also measured and are shown in Figure 3. The feature of the excitation spectrum for $N-P_4-N$ is significantly different from that of $N-P_4$, suggesting that there exist interactions between the chromophores in the ground state. In other words, the excimer originates from a pair of naphthyl groups which exist prior to excitation. The other $N-P_n-N$ studied in the present work show similar behavior and are independent of the linking chain length. All of the observations indicate that the two terminal aryl groups of a molecule of $N-P_n-N$ are included in one supercage, thus giving excimer emission upon excitation. The inclusion of two aromatic chromophores in one supercage of NaY zeolite is now well precedented.[9]

We found that coadsorbed water in the zeolite significantly affects the behavior of the included $N-P_n-N$. Throughout the present work the zeolite used was activated at 500 °C for about 6 h, and only the sample prepared from well-activated zeolite exhibits excimer fluorescence exclusively. The sample prepared from the zeolite which was not thoroughly activated or the one

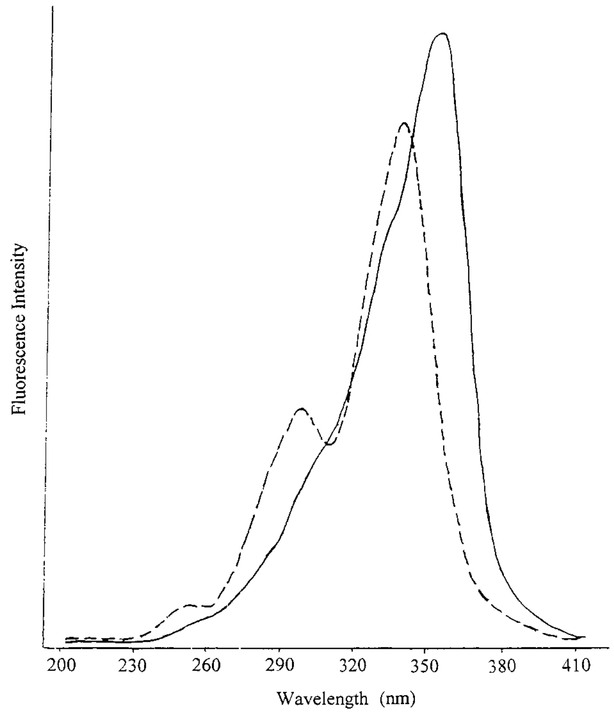


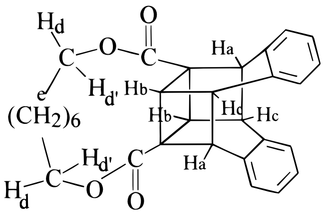
Figure 3. The excitation spectra of N−P_4−N (—) and N−P_4 (- - -) included in NaY zeolite, monitored at λ_{em} = 400 and 370 nm, respectively.

which after activation was allowed to adsorb water mainly shows monomer emission of the naphthyl chromophore (λ_{max} = 370 nm). It is likely that for the sample having coadsorbed water the two terminal groups of one N−P_n−N molecule are not accommodated in one supercage. It has been established that hydration of NaY zeolite causes separation of dimers of the included pyrene.[9b] Accordingly, coadsorbed water also influences the photocycloaddition. For the sample which was not thoroughly activated, the conversion was low even under a long time period of irradiation.

Similarly, photoirradiation of N−M_n−N, which possess polymethylene chains rather than poly(ethylene glycol) chains, adsorbed on NaY zeolite also gives the intramolecular photocyclomers as the unique products as long as the loading level is less than 1 for every 10 supercages. The mass balance is excellent (>95%). Generally, a 4 h irradiation leads to conversion of all the starting materials into the photocyclomers (Table 1). Again, the chain length of N−M_n−N does not show significant effect on their photochemical behavior. The similarity between N−M_n−N and N−P_n−N suggests that the nature of the linking chains in the diaryl compounds does not significantly affect the distribution of the substrate over the supercages provided the chains are conformationally labile. The ^{1}H NMR data for the intramolecular photocyclomer of N−M_8−N are given in Table 3. The largest rings synthesized with the aid of NaY zeolite contain 42 atoms from N−P_{12}−N and the 17 atoms from N−M_{10}−N.

Photocycloaddition of A−M$_n$−A. Photocycloaddition of anthracene and its derivatives has been extensively investigated.[18] In general, photoirradiation of 9-substituted anthracene in organic solution results in [4π + 4π] cycloaddition of the aromatic rings at the 9,10-positions to yield mainly head-to-tail (h−t) rather than head-to-head (h−h) photocyclomers[18b,19] (Scheme 3). This regioselectivity was rationalized in terms of electrostatic and/or steric effects of the substituents.[18a,20] For α,ω-di(9-anthryl)alkanes, it has been established that the compounds may undergo intramolecular [4π + 4π] cycloaddition, but intermolecular [4π + 4π] cycloaddition generally dominates when the linking chains are long and the concentration is high.[5,18a,18f,21−24]

Table 3. ^{1}H NMR Data and Assignments of the Cyclomers of N−M_8−N



N-M$_8$-N

δ (ppm)	split	I	H
6.95−7.00	m	8H	Ar
4.55	d	2H	H_a
4.41	dd	2H	H_c
4.31	m	2H	H_d
4.16	m	2H	$H_{d'}$
3.86	d	2H	H_b
1.50−1.70	m	12H	H_e

As observed in the case of N−P_n−N and N−M_n−N, A−M_n−A included in NaY zeolite with the loading less than 50 μmol g^{-1} (~30 mg of A−M_{10}−A per gram of zeolite) exclusively exhibits intramolecular excimer emission upon excitation. Figure 4 shows the fluorescence spectra of A−M_{10}−A and the model compound 9-anthrylmethyl acetate A_n-CH_2-$OCOCH_3$ (A−M, A_n = 9-anthryl) included in NaY zeolite and in methanol solution. In methanol A−M_{10}−A only exhibits monomer fluorescence with maxima at 395, 420, and 440 nm. However, within the zeolite, while A−M shows monomer fluorescence, A−M_{10}−A only gives excimer fluorescence (λ = 480 nm). Loading dependence measurements of the fluorescence suggests that the excimer is intramolecular. The excitation spectrum for the excimer is evidently red-shifted compared with that of the monomer emission, indicating that the two anthryl chromophores of A−M_{10}−A in the zeolite supercage already are in ground state conformations conducive to easy excimer formation. These results suggest that the two terminal aryl groups of one A−M_{10}−A molecule are included within one supercage of the zeolite. Photoirradiation of the zeolite included A−M_{10}−A only results in intramolecular [4π + 4π] cyclomers. As in the case of N−P_n−N, a molecular model calculation indicates that the photocyclomer of A−M_{10}−A

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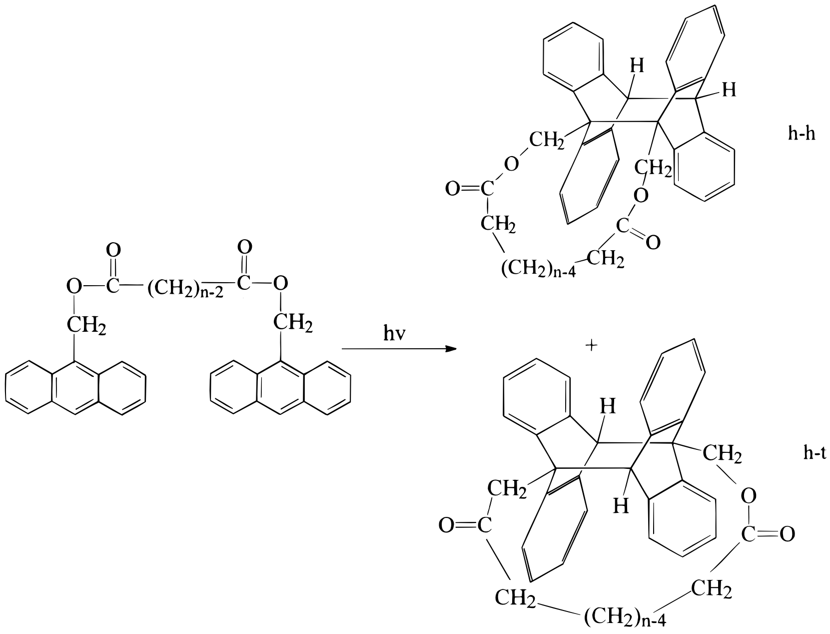
(18) (a) Bouas-Laurent H.; Castellan A.; Desvergne J.-P. *Pure Appl. Chem.* **1980**, *52*, 2633. (b) Cowan D. O.; Drisko R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1976; p 37. (c) Becker H.-D. *Chem. Rev.* **1993**, *93*, 73. (d) Becker H. D.; Langer V.; Becker H.-C. *J. Org. Chem.* **1993**, *58*, 6394. (e) Wolff T.; KlauBner B. *Adv. Colloid Interface Sci.* **1995**, *59*, 31. (f) Bouas-Laurent H.; Desvergne, J.-P. in *Photochromism: Molecules and Systems*; Dürr H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; Chapter 4, p 561. (g) Kaupp, G. In *Advances in Photochemistry*; Neckers, D. C., Volman D. H., von Bunau, G., Eds.; John Wiley & Sons: New York, 1995; Vol. 19, p 119. (h) Mori, Y.; Horikoshi, Y.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1755. (i) Noh T.; Lim H. *Chem. Lett.* **1997**, 495. (j) Tung, C. H.; Guan, J. Q. *J. Org. Chem.* **1998**, in press.

(19) (a) Costa, S. M. B.; Melo, E. *J. Chem. Soc., Faraday Trans. 2,* **1980**, *76*, 1. (b) Cowan, D. O.; Schmiegel, W. W. *J. Am. Chem. Soc.* **1972**, *94*, 6779. (c) Robertson, W. W.; Music, J. F.; Matsen, F. A. *J. Am. Chem. Soc.*, **1950**, *72*, 5260. (d) Yamanoto, S.-A.; Grellmann, K.-H.; Weller, A. *Chem. Phys. Lett.* **1980**, *70*, 241. (e) Yang, N. C.; Shold, D. M.; Kim, B. *J. Am. Chem. Soc.* **1976**, *98*, 6587. (f) Moreno, M. J.; Lourtie, I. M. G.; Melo, E. *J. Phys. Chem.* **1996**, *100*, 18192.

(20) (a) Ito, Y.; Fujita, H. *J. Org. Chem.* **1996**, *61*, 5677. (b) Mori, Y.; Horikoshi, Y.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1996**, 1755.

Scheme 3



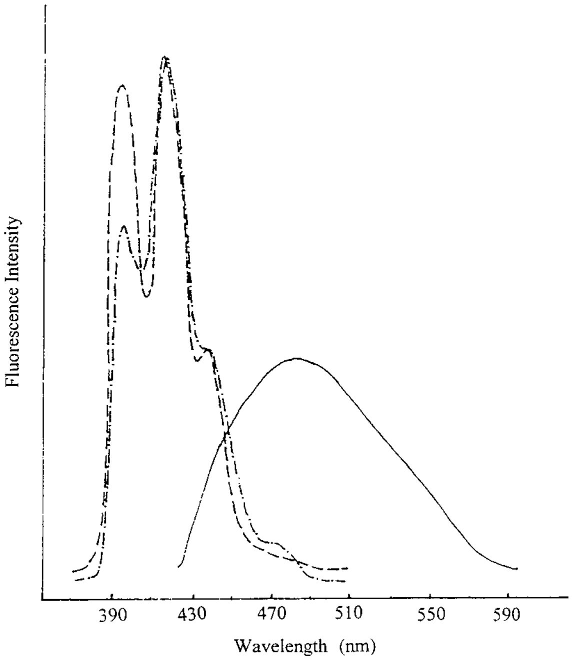


Figure 4. Fluorescence spectra of A−M$_{10}$−A in methanol (1 × 10^{-5} M, - - -) and included in NaY zeolite (10 μmol g^{-1}, —). The fluorescence spectrum of A−M in NaY zeolite is also given (20 μmol g^{-1}, -•-•-). λ_{ex} = 365 nm.

in its lowest energy conformation possesses a size of ca. 8.1 Å × 9.0 Å × 11.3 Å. These photocyclomers are too big to escape form the zeolite supercage through the 7.4-Å window, but still can be accommodated in the supercage. The photocyclomers were isolated by dissolving the zeolite sample with HCl and extracting with ether. No intermolecular cyclomers were detected by HPLC. At the loading above 100 μmol g^{-1}, intermolecular photocyclomer formation was also observed. For example, at a loading of 100 μmol g^{-1} the intermolecular photocyclomer was produced in ca. 5% of the total products. Material balance was above 90%. After 2 h irradiation the conversion of the starting material is close to 100% (Table 1). The structures of the intramolecular photocyclomers were identified by MS and ^{1}H NMR spectroscopy. The assignment of the h−h and h−t photocyclomers relies on the chemical shifts of bridgehead protons in their ^{1}H NMR spectra. It has been established[20,24f] that the chemical shifts of bridgehead protons for h−h cyclomers appear at lower regions compared with those for the corresponding h−t cyclomers. Photoirradiation of A−M$_{10}$−A yields both h−h and h−t intramolecular photocyclomers, with the latter as the major product (h−t/h−h = 4). The ^{1}H NMR data for these photocyclomers are listed in Table 4. They are consistent with literature values for related molecules.[18a,f,21−24] The photocycloaddition of the dianthryl compounds with short linking chains differed from that of A−M$_{10}$−A. Photoirradiation of A−M$_6$−A included in NaY zeolite only gives h−h intramolecular photocyclomer. The ^{1}H NMR data for this cyclomer are listed in Table 5. We followed the photocycloaddition by using fluorescence spectra. After 2 h irradiation, almost all of the starting material was converted to the product. However, when we isolated the product by dissolving the zeolite sample with HCl and extracting with ether, part of the product decomposed, regenerating the starting material. It has been well established that the h−h photocyclomers of 9-substituted anthracenes generally are thermally more labile (regenerating the starting materials) compared with the corresponding h−t cyclomers.[18] This instability of the h−h cyclomers is one of the reasons why their production was rarely observed. Thus, we have examined the stability of the h−h

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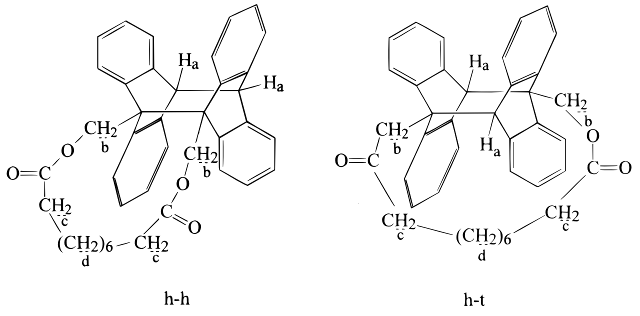
[21] (a) Desvergne, J. P.; Bouas-Laurent, H. *Chem. Commun.* **1978**, 403 (b) Desvergne, J. P.; Fages, F.; Bouas-Laurent, H.; Marsau, P. *Pure Appl. Chem.* **1992**, *64*, 1231 (c) Castellan, A.; Desvergne, J. P.; Bouas-Laurent, H. *Chem. Phys. Lett.* **1980**, *76*, 390.

[22] (a) Fox, M. A.; Britt, P. F. *J. Phys. Chem.* **1990**, *94*, 6351. (b) Fox, M. A.; Britt, P. F. *Photochem. Photobiol.* **1990**, *51*, 129.

[23] (a) Kaupp, G.; Teufel, E. *Chem. Ber.* **1980**, *113*, 3669. (b) Wolff, T. *J. Photochem.* **1981**, *16*, 343. (c) Wolff, T.; Muller, N.; von Bunau G. *J. Photochem.* **1983**, *22*, 71. (d) Wolff, T.; Muller, N. *J. Photochem.* **1983**, *23*, 131. (e) Schutz, A.; Wolff, T. *J. Photochem. Photobiol. A, Chem.* **1997**, *109*, 251.

[24] (a) Becker, H. D.; Amin, K. A. *J. Org. Chem.* **1989**, *54*, 3182. (b) Becker, H. D.; Elebring, T.; Sandros, K. *J. Org. Chem.* **1982**, *47*, 1064. (c) Ferguson, J. *Chem. Phys. Lett.* **1980**, *76*, 398. (d) Jones, G., Bergmark, W. R.; Halpern, A.M. *Chem. Phys. Lett.* **1980**, *76*, 403. (e) De Schryver, F. C.; Boens, N.; Huybrechts, J.; Daemen, J.; De Brackeleire, M. *Pure Appl. Chem.* **1977**, *49*, 237. (f) Ito, Y.; Olovsson, G. *J. Chem. Soc., Perkin Trans. 1* **1997**, 127.

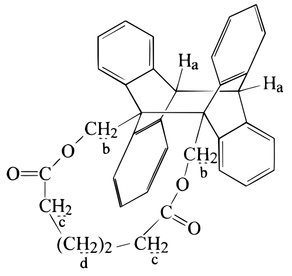
Table 4. ^{1}H NMR Data and Assignments of the Cyclomers of A−M$_{10}$−A



A-M$_{10}$-A

δ (ppm)	split	I	H
Photocyclomer of A−M$_{10}$−A (h−h)			
6.80−7.00	m	16H	Ar
5.21	s	4H	H$_b$
3.77	s	2H	H$_a$
2.15	t	4H	H$_c$
1.25	m	12H	H$_d$
Photocyclomer of A−M$_{10}$−A (h−t)			
6.80−7.00	m	16H	Ar
5.14	s	4H	H$_b$
4.47	s	2H	H$_a$
2.35	t	4H	H$_c$
1.25	m	12H	H$_d$

Table 5. ^{1}H NMR Data and Assignments of the Cyclomers of A−M$_6$−A



A-M$_6$-A

δ (ppm)	split	I	H
6.80−7.00	m	16H	Ar
5.20	s0	4H	H$_b$
3.75	s	2H	H$_a$
2.16	t	4H	H$_c$
1.25	m	4H	H$_d$

cyclomers and compared it with the h−t cyclomer. The photocyclomers for A−M$_6$−A and A−M$_{10}$−A in chloroform-*d* were stored in the dark at room temperature, and the regenerated starting materials were checked at intervals by quick UV measurements. It was found that the h−h cyclomers for A−M$_6$−A and A−M$_{10}$−A decomposed within 1 day on storage in the dark at room temperature, regenerating the starting materials, while the h−t cyclomer of A−M$_{10}$−A underwent no decomposition over a period of 3 weeks.

Intramolecular Photocycloaddition of N−P$_n$−A. Although the photocycloaddition of anthracene[18] and that of naphthalene[6,15] have been extensively studied, until recently relatively little has been reported on the cross-photocycloaddition between an anthracene and a naphthalene moiety.[25−29] The main reason for this is the large difference in the quantum yields between the photocycloaddition of anthracene and the cross-photocycloaddition of anthracene and naphthalene. Thus, bichromophoric molecules with anthryl as one chromophore and naphthyl as the other generally undergo intermolecular anthryl−anthryl cycloaddition rather than intramolecular cross-cycloaddition when irradiated.

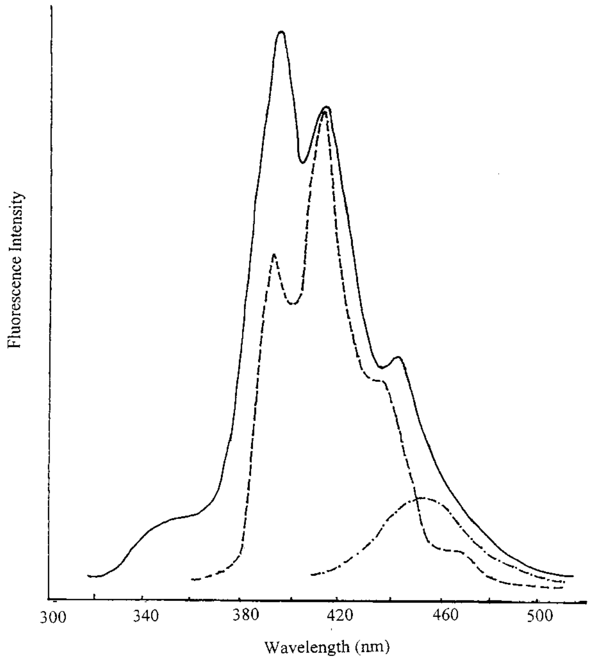


Figure 5. Fluorescence spectra of N−P$_4$−A (— excitation at 280 nm) and A−M (- - - excitation at 365 nm) included in NaY zeolite. Exciplex emission spectrum (-•-•-) is derived by subtraction of spectrum of A−M from that of N−P$_4$−A normalized at 420 nm. The loading level are 10 μmol g^{-1}.

Chandross and Schiebel were the first to study the photochemical processes of 1-(9-anthryl)-3-(1-naphthyl)propane (ANP) in which the two chromophores are separated by three saturated carbon atoms, thus offering the best geometrical relationship for the observation of excited-state interactions.[25] Irradiation of 2×10^{-5} M ANP in organic solvents gave the intramolecular $[4\pi + 4\pi]$ cyclomer, while irradiation at concentrations $>10^{-3}$ M resulted in intermolecular $[4\pi + 4\pi]$ cycloadditions involving two anthracene moieties. However, intramolecular cyclomers could not be isolated. Ferguson, Mau, and Puza studied the photochemistry of ANP in more detail.[26] They characterized the structure of the intramolecular photocyclomer by NMR spectroscopy and X-ray diffraction. Later on, Bouas-Laurent and co-workers studied the intramolecular photocycloaddition of 9-(1-naphthylmethoxymethyl)anthracene and found that the photocycloaddition quantum yield is 10 times higher than that of ANP.[27] Albini and co-workers used the charge-transfer interactions of 9-cyanoanthracene with naphthalene and 2-cyanonaphthalene with anthracene to synthesize the cross-cy-

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(25) (a) Chandross, E. A.; Schiebel A. H. *J. Am. Chem. Soc.* **1973**, *95*, 611. (b) Chandross E. A.; Schiebel, A. H. *J. Am. Chem. Soc.* **1973**, *95*, 1671.

(26) (a) Ferguson, J.; Mau, A. W.-H.; Puza, M. *Mol. Phys.* **1974**, *27*, 377. (b) Ferguson, J.; Mau, A. W.-H.; Puza, M. *Mol. Phys.* **1974**, *28*, 1457. (c) Ferguson, J.; Mau, A. W.-H.; Whimp, P. O. *J. Am. Chem. Soc.* **1979**, *101*, 2370.

(27) Desvergne, J. P.; Bitit, N.; Castellan, A.; Bouas-Laurent, H. *J. Chem. Soc., Perkin. Trans. 2* **1983**, 109.

(28) (a) Albini, A.; Fasani, E.; Faiardi, D. *J. Org. Chem.* **1987**, *52*, 155. (b) Albini, A.; Fasani, E. *J. Am. Chem. Soc.* **1988**, *110*, 7760.

(29) (a) Shinmyozu, T.; Inazu T.; Yoshino, H. *Chem. Lett.* **1978**, 405. (b) Tazuke, S.; Watanabe, H. *Tetrahedron Lett.* **1982**, *23*, 197. (c) Ferguson, J.; Puza, M.; Robbins, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1869. (d) Usui, M.; Shindo, Y.; Hida, M. *Nippon Kagaku Kaishi* **1991**, 206.

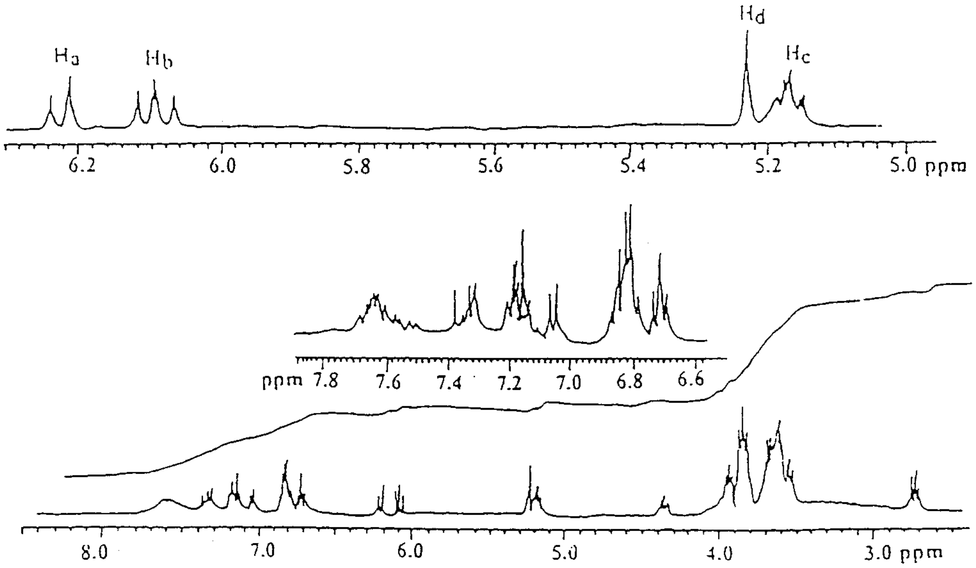
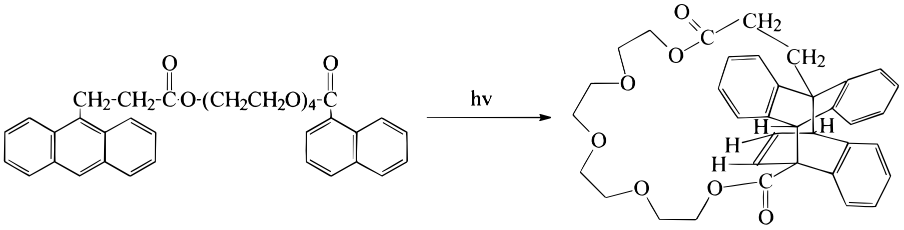


Figure 6. 400-MHz ^{1}H NMR spectrum of the intramolecular cyclomer of N−P$_4$−A in CD$_3$COCD$_3$.

Scheme 4



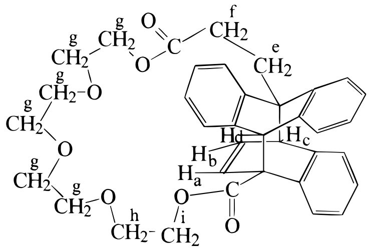
clomer.[28] Furthermore, the cross-cycloaddition between anthracene and naphthalene moieties in diaza[3,3](1,4)naphthaleno-(9,10)anthracenes and cyclophanes has been reported.[29] In these molecules, the anthracene and naphthalene chromophores are fixed as a sandwich pair.

The difficulty of synthesis of naphthalene−anthracene cross-photocyclomers can be overcome by irradiation of bichromophoric compounds included in Y-type zeolites. Figure 5 shows the fluorescence spectra of N−P$_4$−A and the model compound for anthryl (A−M) included in NaY zeolite with the loading of 10 μmol g^{-1}. As mentioned in the above section, A−M only exhibits monomer fluorescence with maxima at 395, 420, and 440 nm upon excitation at 365 nm. On the other hand, selective excitation of the naphthyl group in N−P$_4$−A at $\lambda = 280$ nm mainly results in the emission of the anthryl chromophore, although weak fluorescence from the naphthyl is observed. The excitation spectrum for the anthryl fluorescence corresponds to the UV absorption both of the anthryl and the naphthyl chromophores. These observations suggest that significant energy transfer from naphthyl to anthryl occurs. Furthermore, in addition to the anthryl monomer emission the fluorescence spectrum of N−P$_4$−A shows a long tail extending to the lower energy. Since the (0,0) band (at 395 nm) of the anthryl emission overlays on the fluorescence of the naphthyl ($\lambda_{max} = 370$ nm), we normalized the second vibronic band (at 420 nm) of the N−P$_4$−A emission spectrum to that of A−M. Subtraction of the A−M spectrum from the spectrum of N−P$_4$−A results in the exciplex emission. The exciplex fluorescence between anthryl and naphthyl chromophores has been reported by Chandross,[25] Ferguson,[26] and Bouas-Laurent[27] for 1-(9-anthryl)-3-(1-naphthyl)propane and 9-(1-naphthylmethoxymethyl)anthracene in solid state and in solution, respectively. Even at very low loading levels (<5 μmol g^{-1}) N−P$_4$−A shows exciplex emission, suggesting that the exciplex is intramolecular. Therefore, we infer that the two terminal groups of an N−P$_4$−A molecule are included in one supercage of the zeolite, thus enhancing the energy transfer and exciplex formation. Irradiation of 1×10^{-3} M N−P$_n$−A in acetonitrile gives the intermolecular photocyclomer of two anthracene groups. On the other hand, below 1×10^{-3} M, irradiation results in no photochemical reaction, because the lifetime of the singlet excited state of the anthryl (or naphthyl) is not long enough to allow it to encounter the other terminal chromophore of the N−P$_n$−A molecule (intramolecular reaction) or a chromophore of another molecule (intermolecular reaction). However, irradiation of N−P$_n$−A adsorbed on NaY zeolite with loading levels below 50 μmol g^{-1} yields the intramolecular [$4\pi + 4\pi$] photocyclomer exclusively (Scheme 4). A molecular model calculation shows that the photocyclomer of N−P$_4$−A in the conformation with the lowest energy has a size of ca. 8.3 Å × 8.8 Å × 11.3 Å. Thus, this photocyclomer cannot escape form the supercage through the 7.4-Å window. As in the case of N−P$_n$−N, N−M_n−N, and A−M_n−A, these photocyclomers were easily isolated by dissolving the zeolite framework with concentrated HCl followed by extraction with ether. The mass balance was $>$90%, suggesting that any unidentified products must be minor. N−P$_3$−A and N−P$_5$−A show similar behavior (Table 1), suggesting that the linking chain length does not affect the photocycloaddition significantly. The ^{1}H NMR spectrum for the cross-photocyclomer of N−P$_4$−A, which is consistent with that reported by Ferguson, Mau, and Puza,[26] is shown in Figure 6; spectral details and assignments are given in Table 6.

Conclusion

Supercages of Y-type zeolites can include diaryl molecules with flexible linking chains when the aryl groups are anthryl or naphthyl and the chains are poly(ethylene glycol) or polymethylene. Since one of these molecules can fit almost

Table 6. ^1H NMR Data and Assignments of the Cyclomers of N−P_4−A



N-P_4-A

δ (ppm)	split	I	H
6.60−7.50	m	12H	Ar
6.22	d	1H	H_a
6.10	m	1H	H_b
5.23	s	1H	H_d
5.18	m	1H	H_c
4.35	t	2H	H_i
4.01	t	2H	H_f
3.85	t	2H	H_h
3.75−3.50	m	12H	H_g
2.85	t	2H	H_e

completely in a host supercage, another molecule cannot enter. At loading levels less than 1 molecule per 10 supercages, the calculated probability to find 2 molecules in two neighboring supercages is very small. Thus, the substrate molecules are isolated from each other by the supercages. N−P_n−N, N−M_n−N, and A−M_n−A exclusively exhibit excimer fluorescence. Selective excitation of the naphthyl group in N−P_n−A results in the anthryl emission and exciplex fluorescence. These observations suggest that the substrate molecules have their two terminal groups compartmentalized in one supercage. As a result, irradiation of such inclusion compounds gives intramolecular photocyclomers exclusively. Hence, Y-type zeolites can be used as microreactors to synthesize large-ring compounds without competition from intermolecular reaction even at loadings of tens of milligrams of substrate per gram of zeolite. By inclusion of N−P_n−A in NaY zeolite, even cross-photocyclomers of naphthalene and anthracene moieties can be synthesized efficiently.

Experimental Section

Materials and Instruments. Spectral-grade acetonitrile, cyclohexane, and dichloromethane were used without further purification for inclusion of substrates within zeolite and for extraction of products from zeolite, respectively. Samples of NaY zeolite were purchased from Nankai University and heated in a furnace at 500 °C in air for about 6 h. Naphthalene end-labeled poly(ethylene glycol) (N−P_n−N),[6b] polymethylene bis(2-naphthoate) (N−M_n−N),[6a] and 9-anthrylmethyl α,ω-alkanedioates (A−M_n−A)[30] were prepared as reported previously. α-(9-Anthryl)-ω-(1-naphthyl) end-labeled poly(ethylene glycol) (N−P_n−A) were synthesized by esterification of poly(ethylene glycol) first with 1-naphthoyl chloride and then with anthracene-9-propionic acid. For example, N−P_4−A was prepared as follows: To a solution of tetraethylene glycol (2.5 g, 13 mmol) in dry tetrahydrofuran (THF, 20 mL) was added first pyridine (2 mL) and then the solution of 1-naphthoyl chloride (2 g, 11 mmol) in THF (7 mL) with vigorous stirring under refluxed temperature. The mixture was refluxed for 10 h and then cooled. The resulting pyridine hydrochloride was removed by filtration. Evaporation of the solvent afforded a yellow oil product, one-end-labeled tetraethylene glycol (N−P_4). The product was purified by column chromatography on silica eluted with petroleum ether/diethyl ether (25/75 in volume), yield 2.92 g (80%). The mixture of N−P_4 (0.85 g, 2.46 mmol), anthracene-9-propionic acid (0.5 g, 1.97 mmol), 1,3-dicyclohexylcarbodiimide (2 g), and a catalytic amount of *p*-toluenesulfonic acid was refluxed for 12 h and then cooled and mixed with 150 mL water. The mixture was neutralized to pH = 7 with 6 N HCl. A yellow precipitate was separated by filtration and was extracted with dichloromethane. The dichloromethane solution was dried with anhydrous $MgSO_4$. Evaporation of the solvent afforded a yellow oil product N−P_4−A. The product was purified by chromatography on a silica plate eluted with petroleum ether/diethyl ether (25/75 in volume), yield 0.3 g (30%). The analysts data are given in the Supporting Information.

^1H NMR spectra were recorded at 400 MHz with a Varian XL-400 spectrometer. MS spectra were run on a VG ZAB spectrometer. UV spectra were measured with a Hitachi UV-340 spectrometer. Photocycloaddition products were separated and analyzed by using a Varian VISTA 5500 liquid chromotograph with a Lichrosorb RP18 column.

Inclusion of Substrates within Zeolites and Photoirradiation. Weighted amounts of the substrates and the activated NaY zeolite were stirred together in cyclohexane. In a typical preparation 500 mg of the zeolite and 10−20 mg of the substrate were taken in 20 mL of the solvent. After stirring for about 10 h, the sample was isolated by filtration and washed with ether twice and dried under nitrogen. This sample was then transferred to a quartz cell equipped with a vacuum stopcock. The sample was degassed thoroughly (10^{-4} mmHg) and photoirradiated with a 450-W Hanovia high-pressure mercury lamp. Neat toluene was used as a filter. The cell was tumbled continuously to provide uniform exposure. After irradiation, the sample was washed with dichloromethane thoroughly until no substrate in the extraction solution could be detected by UV absorption. Then the zeolite was dissolved with concentrated HCl and extracted with ether or dichloromethane. Control experiments established that the products are stable to the acid extraction conditions. After evaporation of ether, pure products were generally obtained as analyzed by HPLC. Structures of all the products were identified by MS and ^1H NMR spectra. Representative spectral data have been given in the Results and Discussion. The detail of the analysis data for the starting materials and photocyclomers are given in the Supporting Information.

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Supporting Information Available: IR, ^1H NMR, and mass spectral data of N−P_4−N, N−P_5−N, N−P_{10}−N, N−P_{12}−N, N−M_3−N, N−M_5−N, N−M_8−N, N−M_{10}−N, A−M_6−A, A−M_{10}−A, N−P_3−A, N−P_4−A, and N−P_5−A and their photocyclomers (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(30) Tung, C.-H.; Li, Y. *J. Chin. Chem.* **1995**, *13,* 532.