Supplementary Information for *Chem. Commun.*

An Extremely Stable, Self-Complementary Hydrogen-Bonded Duplex

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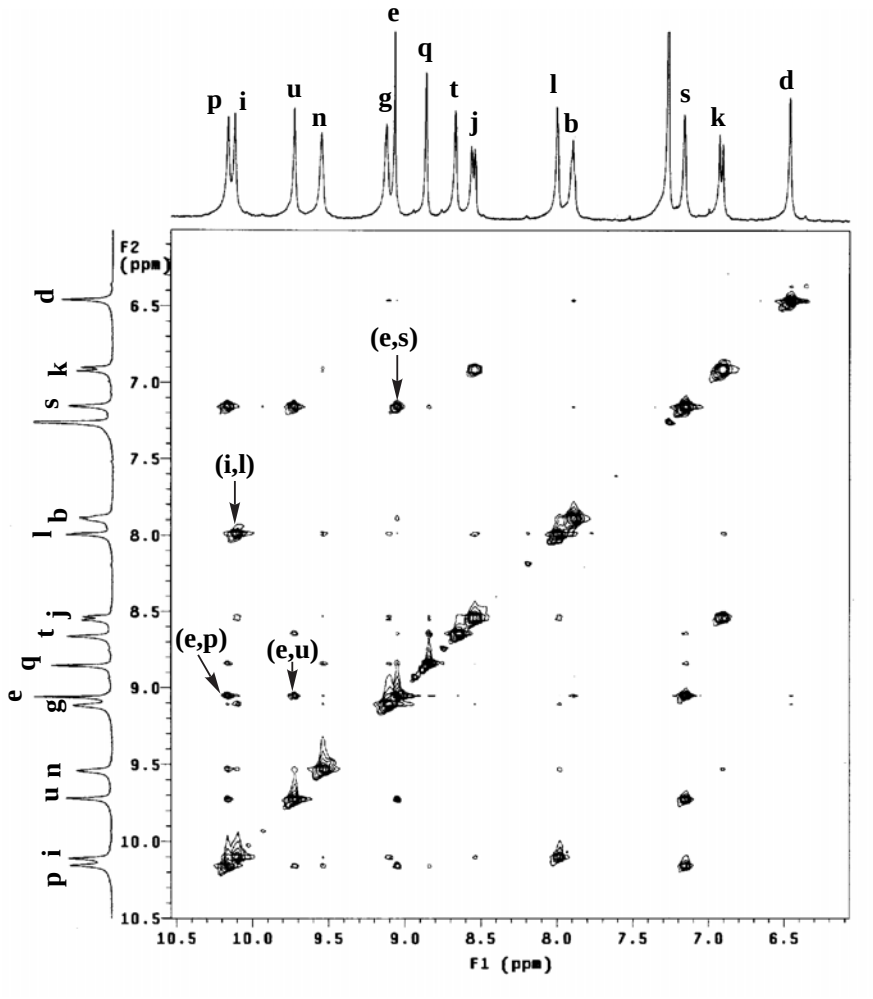
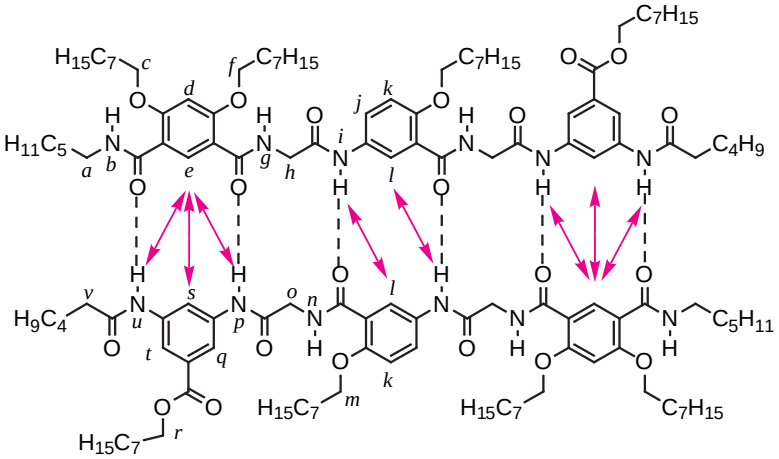
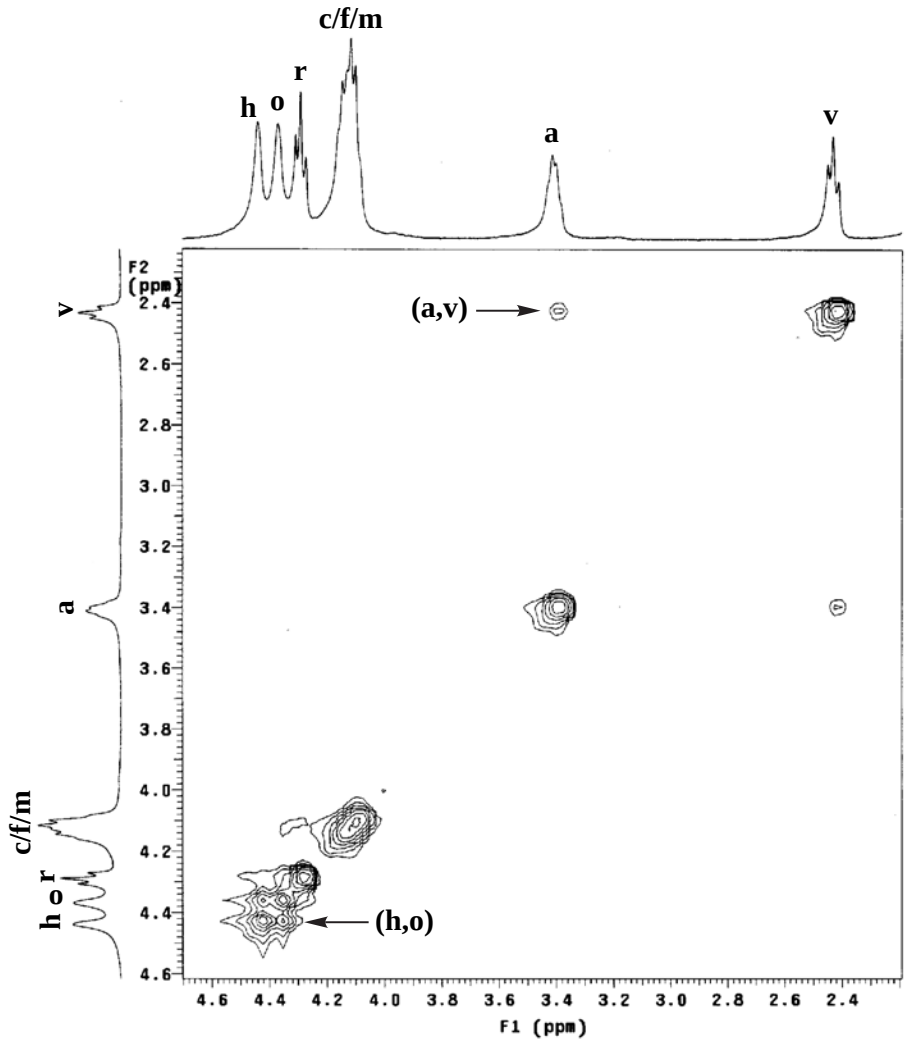
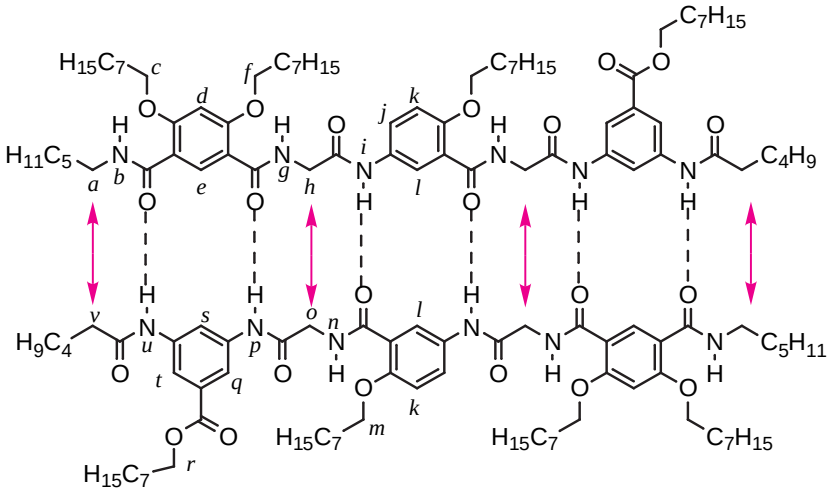
I. 2D ^{1}H NMR Spectra of 3•3









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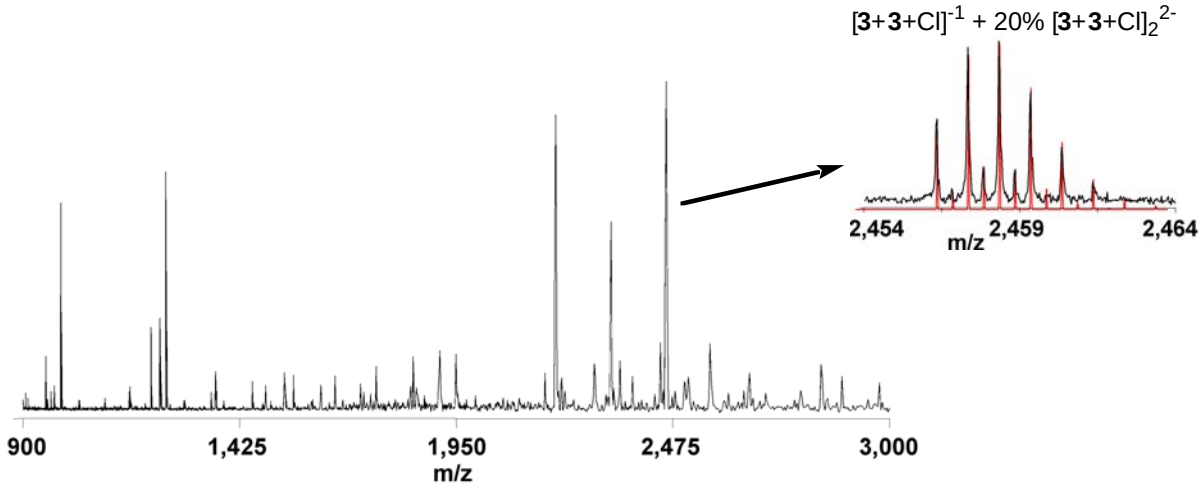
II. Mass Spectrometry Experiment

ESI-FTICR mass spectra were acquired using the 7 tesla FTICR mass spectrometer [1] equipped with an Odyssey data system (Finnigan FTMS, Madison, WI). Complexes were dissolved in chloroform at 1 mM with 1 mM tetraphenylphosphonium chloride (Ph_4PCl) [2]. The solution was directly infused into the ion source of the mass spectrometer. Ions were transferred from the ESI interface to the trap using a rf-quadrupole for collisional focusing at 200 mTorr, followed by two sets of rf-only quadrupoles in the higher vacuum region of the mass spectrometer. Negative ion mass spectra were acquired using a standard experimental sequence for ion injection and accumulation, pump-down, excitation, and detection. The total spectrum acquisition time was about 4 s. Ion accumulation was accomplished by injecting 10^{-5} Torr of N_2 into the trap *via* a piezoelectric pulse valve (Lasertechniques Inc., Albuquerque, NM). Background pressure in the ICR trap was maintained at 10^{-9} Torr using a custom cryopumping assembly [1]. The mass spectrum is shown below.

[1] B. E. Winger, S. A. Hofstadler, J. E. Bruce, H. R. Udseth, R. D. Smith, *J. Am. Soc. Mass Spectrom*. 1993**, 4**, 566-577.

[2] X. Cheng, Q. Gao, R. D. Smith, E. E. Simanek, M. Mammen, G. M. Whitesides, *Rapid Comm. Mass Spectrom.* 1995, 9, 312-316.

(Tetraphenylphosphonium chloride, 98%, Aldrich, Milwaukee, WI)
(Chloroform, 99.8%, Acros Organics, New Jersey)

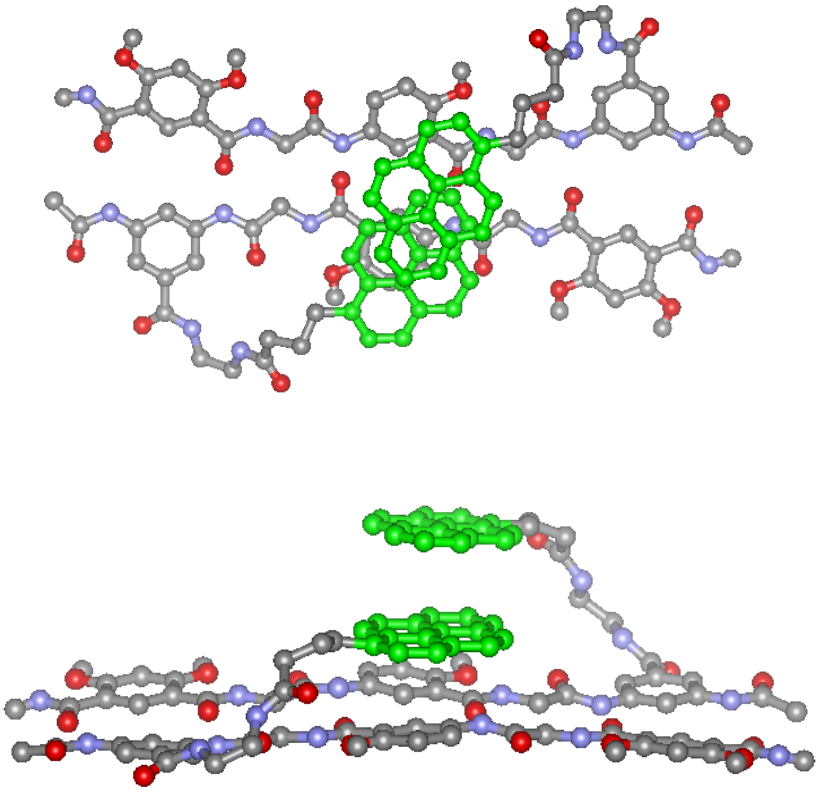


III. Fluorescence Experiments and Emission Spectra of 3' at Various Concentrations

Fluorescence emission spectra were measured with a Perkin-Elmer LS55 luminescence spectrometer set to an excitation wavelength of 411 nm. The chloroform used for fluorescence spectroscopy was of spectrophotometric grade and was used as received. All fluorescence measurements were obtained at room temperature in luminescence spectroscopy cells with a 1.00-cm path length. The emission band of the pyrene monomer was detected at 450 nm and that of the excimer appeared at 510 nm. Concentration-dependent changes of the ratio Ie/Im, defined as the ratio between the intensities of the excimer emission band and the monomer emission band, started to appear with $\leq 10^{-9}$ M and were plot against concentration. The data was fitted into a dimerization equation described before by Wilcox[1].

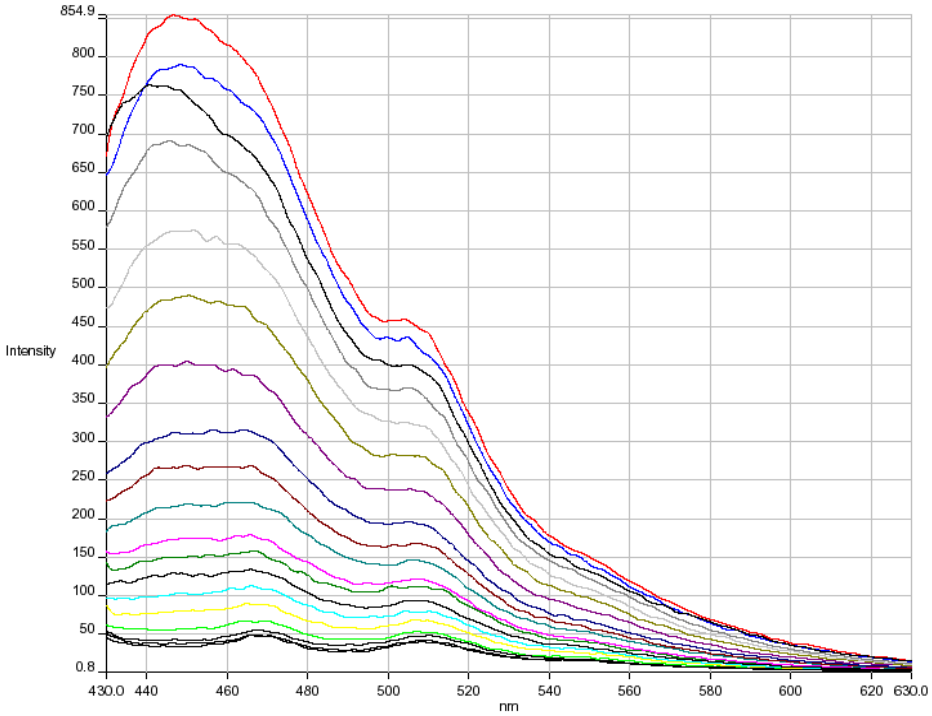
1. C. S. Wilcox, In *Frontiers in Supramolecular Organic Chemistry and Photochemistry.* Schneider, H.-J. and Durr, H., Eds. VCH: New York, 1991.

Molecular model of 3'•3'
(all side chains except for the pyrene moieties are replaced with methyls)

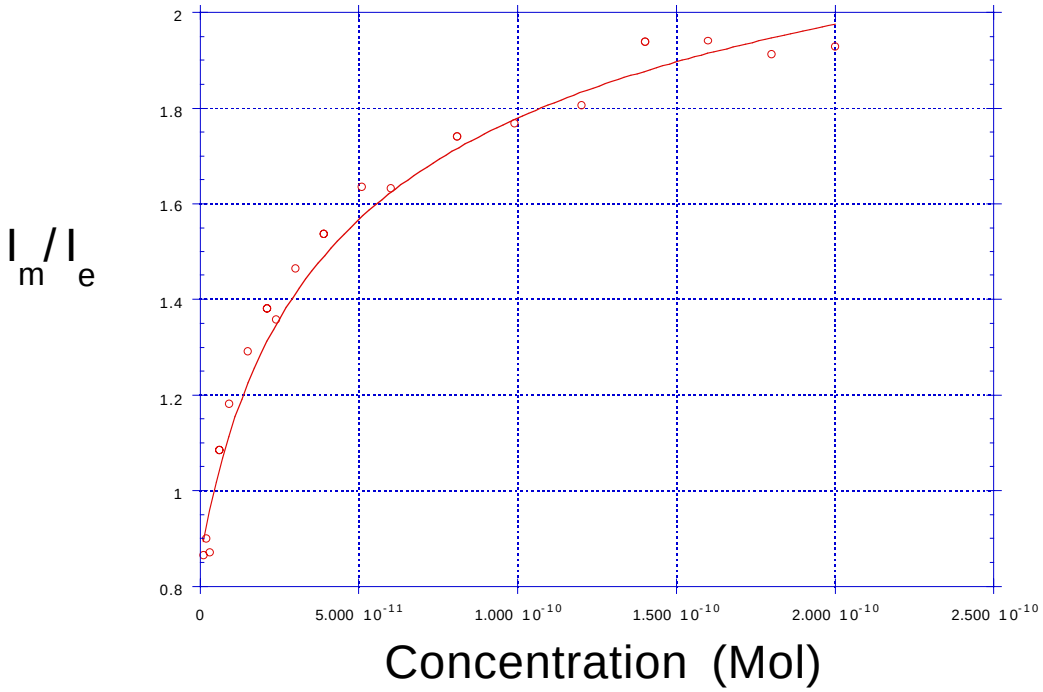


The the linkers are long enough to bring the pyrene groups into close proximity. This model was generated with CS Chem3D Pro, v. 4.0 and displayed using WebLab ViewerLite 3.2.

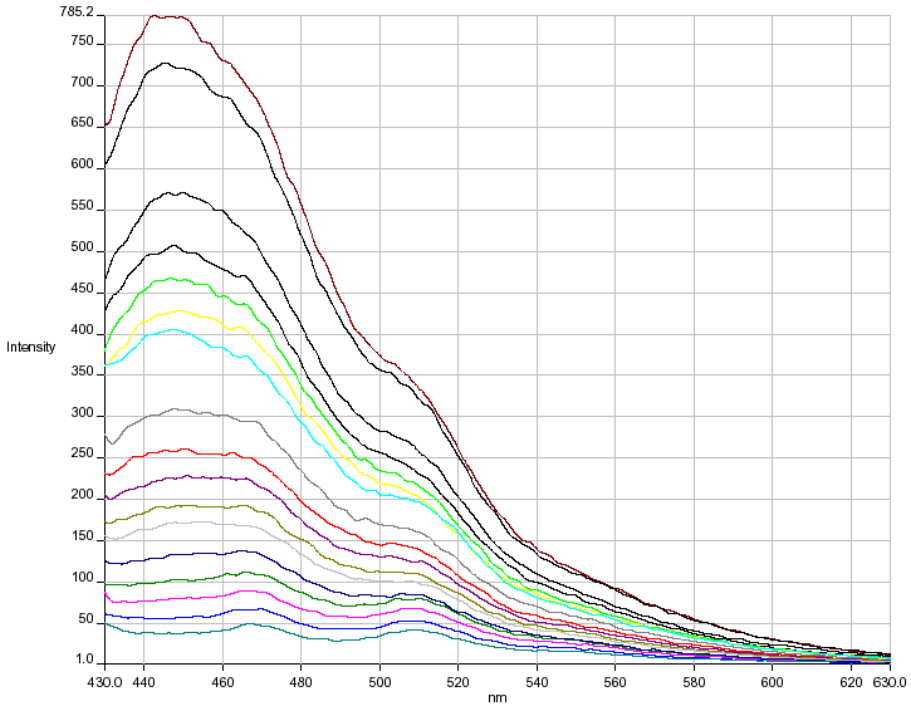
Fluorescence emission spectra (λ_{ex} = 411 nm) of the pyrene-labeled dimer in the concentration range of 10^{-10} to 10^{-8} M in chloroform.



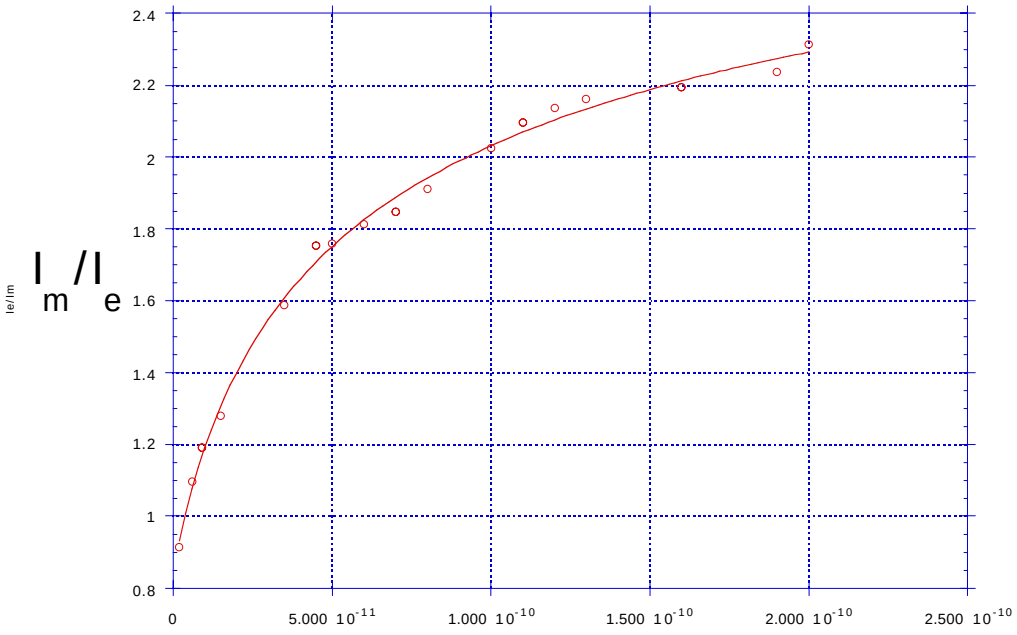
Monomer to Excimer Intensity Ratio of Pyrene-labeled Dimer as a Function of Concentration



Fluorescence emission spectra (λ_{ex} = 411 nm) of the pyrene-labeled dimer in the concentration range of 10^{-10} to 10^{-8} M in chloroform.



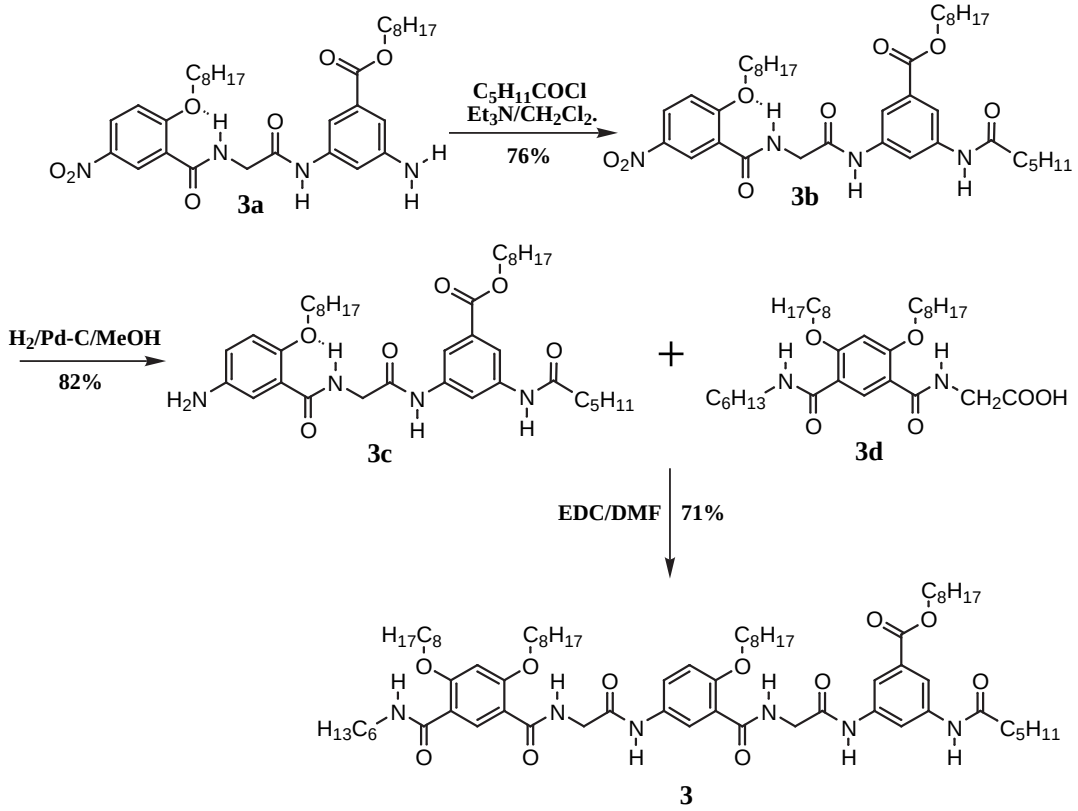
Monomer to Excimer Intensity Ratio of Pyrene-labeled Dimer as a Function of Concentration



IV. Synthetic Procedures

General

All chemicals were purchased from Aldrich or Acros and were used as received unless otherwise noted. Triethylamine was dried from sodium and degassed before use. The coupling reactions were carried out under dry argon. All reactions were followed by thin-layer chromatography (precoated 0.25 mm silica gel plates from Aldrich), and silica gel column chromatography was carried out with silica gel 60 (mesh 230-400). The ^{1}HNMR spectra and ^{13}C NMR were recorded on a 400 MHz spectrometer. NMR chemical shifts are reported in ppm relative to internal standard TMS, and coupling constant, *J*, is reported in Hertz (Hz). The following splitting patterns are designed as s, singlet; d, double; t, triplet; q, quartet; b, broad; m, multiplet.



Octyl 3-hexanoamido-5-[(5'-nitro-2'-octyloxy)phenylcarbonylamino methyl-carbonylamino]-benzoate (3b): Compound **3a** (0.850 g, 1.22 mmol) was dissolved in the hot mixture of CH_2Cl_2 (15 mL) and DMF (10 mL), to which hexanoyl chloride (0.208 g, 1.50 mmol) in CH_2Cl_2 (5 mL) was added drop by drop. The reaction mixture was kept stirring for 6 hrs. The solvent was removed in *vacuo* , and distilled water (50mL) was added. The resulting precipitated solid was filtered off and washed with CH_2Cl_2 to give pure **3b** as a white solid (0.646 g, 76%). ^{1}HNMR (DMSO-d_6) δ 0.76-0.86 (m, 9H), 1.15-1.68 (m, 26H), 1.86 (m, 2H), 2.29 (t, 2H, J = 7.2), 4.19-4.29 (m, 6H), 7.40 (d, 1H, J = 9.2), 7.89 (s, 1H), 8.01 (s, 1H), 8.20 (s, 1H) 8.35 (q, 1H, J = 2.4, 9.2), 8.63 (d, 2H, J = 2.8), 10.10 (s, 1H), 10.36 (s, 1H). ^{13}CNMR (DMSO-d_6) δ 13.86, 13.89, 13.92, 21.91, 22.08, 24.75, 25.45, 25.61, 28.19, 28.261, 28.64, 28.74, 30.86, 31.22, 36.37, 64.74, 70.30, 114.05, 114.31, 122.31,

122.56, 126.36, 128.08, 130.57, 139.32, 139.97, 140.50, 161.55, 162.85, 165.51, 167.22, 171.59.

Octyl 3-hexanoamido-5-[(5'-amino-2'-octyloxy)phenylcarbonylamino methyl-carbonylamino]-benzoate (3c): Hydrogenation of **3b** gave crude product **3c** (82%), which was used directly for the next step without further purification. ^{1}HNMR (DMSO-d_6) δ 0.75 (t, 3H, J = 6.4), 0.81-0.86 (m, 6H), 1.14-1.38 (m, 24H), 1.58 (m, 2H), 1.68 (m, 2H), 1.85 (m, 2H), 2.30 (t, 2H, J = 7.2), 4.16-4.20 (m, 4H), 4.24 (m, 2H), 7.28 (d, 1H, J = 9.2), 7.45 (q, 1H, J = 2.4, 8.8), 7.88 (q, 2H, J = 2.8, 7.2), 8.03 (s, 1H), 8.19 (s, 1H), 8.67 (t, 1H, J = 2.8), 9.95 (b, 2H), 10.14 (s, 1H), 10.40 (s, 1H). ^{13}CNMR (DMSO-d_6) δ 13.85, 13.87, 13.91, 21, 88, 22.03, 22.06, 24.74, 25.42, 25.74, 28.18, 28.43, 28.58, 28.61, 28.71, 28.76, 30.84, 31.92, 36.35, 43.57, 64.73, 69.61, 113.89, 114.33, 114.60, 114.69, 122.13, 124.90, 125.85, 126.77, 130.57, 139.32, 139.96, 155.61, 163.51, 165.51, 167.33, 171.60

Octyl 3-hexanoamido-5-[(5'-((5-hexanoamido –2,4-dioctyloxy) phenyl carbonylamino methyl-carbonylamino)-2'-octyloxy)phenylcarbonylamino methyl-carbonylamino]-benzoate (3): To a solution of acid **3d** (0.163 g, 0.29 mmol) and EDC (0.056 g, 0.29 mmol) and HOBt (0.039 g, 0.29 mmol) in DMF (25 mL) was added amine **3c** (0.193 g, 0.29 mmol). The reaction mixture was allowed to proceed for 6 hrs at room temperature. The precipitate was filtered off to give pure **3** as a white solid (0.249 g, 71%). ^{1}HNMR ($CDCl_3$) δ 0.80-0.91 (m, 18H), 1.24-1.54 (m, 48H), 1.63-1.68 (m, 4H), 1.78-1.82 (m, 4H), 2.01-2.05 (m, 4H), 2.42 (t, 2H, J = 4.8), 3.39 (m, 2H), 4.08-4.13 (m, 8H), 4.29 (t, 4H, J = 7.2), 4.40 (s, 2H), 6.45 (s, 1H), 6.89 (d, 1H, J = 9.2), 7.14 (s, 1H), 7.89 (t, 1H, J = 3.6), 7.97 (s, 1H), 8.54 (q, 1H, J = 2.8, 8.8), 8.67 (s, 1H), 8.85 (s, 1H), 9.05 (s, 1H), 9.11 (s, 1H), 9.53 (s, 1H), 9.72 (s, 1H) 10.09 (s, 1H), 10.14 (s, 1H). ^{13}CNMR ($CDCl_3$) δ 172.41, 166.70, 166.63, 166.30, 164.60, 164.50, 163.75, 161.38, 160.56, 153.76, 139.38, 139.31, 136.13, 132.53, 131.67, 124.52, 121.29, 120.20, 113.71, 112.86, 96.51, 70.43, 69.93, 69.71, 65.07, 40.45, 36.92, 32.06, 31.86, 31.83, 31.81, 31.72, 31.67, 29.56, 29.52, 29.50, 29.47, 29.36, 29.33, 29.30, 29.26, 28.97, 28.80, 27.08, 26.48, 26.38, 26.28, 25.95, 25.18, 22.73, 22.71, 22.66, 14.20, 14.10, 14.07, 14.02, 14.01. Anal. Calcd. for $C_{70}H_{110}N_6O_{11}$: C, 69.39; H, 9.15; N, 6.94; Found: C, 69.19; H, 9.14; C, 6.96.