

Supporting Information

Nonlinear Optical Properties and Excited-State Dynamics of Highly Symmetric Expanded Porphyrins

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Contents

	Page
Preparation of 1-7	S3~6
Molecular Extinction Coefficient of 1-7	S7
Schematic conjugation pathways and NICS(0) values of 1-7	S8
S ₁ -state decay profiles of 1-7	S9
T ₁ -state decay profiles of 3, 5, and 6	S10
Open-aperture femtosecond Z-scan traces of 3-7	S11

Preparation of **1**

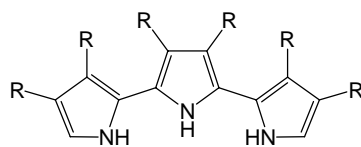
A solution of pentafluorobenzaldehyde (494 μL , 4 mmol) and pyrrole (278 μL , 4 mmol) in 60 mL of dichloromethane was placed in 100 mL of round-bottomed flask under nitrogen. To the solution, 100 μL of 2.5 M BF_3OEt_2 in dichloromethane was added, and the resulting solution was stirred for 2 h. After addition of DDQ (2.27 g, 10 mmol), the solution was stirred for 10 h, and passed through a short alumina column. **1** was separated from the reaction mixture by silica gel column chromatography in 18% yield (176 mg).

Preparation of **2**

Excess amount of NaBH_4 was added to a solution of **1** in a mixture of dichloromethane and methanol and the resulting solution was stirred for 10 min under nitrogen. After removing the solvent, the residue was dissolved in CH_2Cl_2 , and filtered through a short alumina column to give **2** quantitatively.

Preparation of **3**

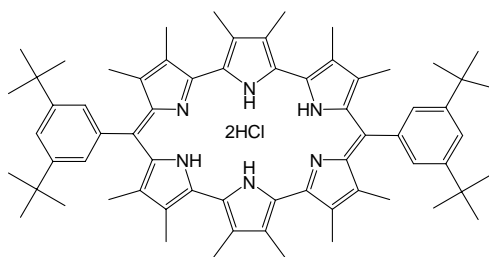
To a solution of *meso*-pentafluorophenyl substituted tripyrrane (450 mg, 0.81 mmol) in 90 mL of CH_2Cl_2 was added TFA (30.6 μL , 0.4 mmol) and the resulting solution was stirred for 90 min at room temperature under a nitrogen atmosphere. Then chloranil (594 mg, 2.63 mmol) was added and the mixture was refluxed for a further 90 min. The reaction was quenched with aqueous NaHCO_3 solution, and the organic layer was washed once with water, and dried over anhydrous Na_2SO_4 . After removal of solvent, the crude product was purified over a neutral alumina column using a mixture of CH_2Cl_2 /hexane as an eluent. After elution of deeply colored fractions, a purple fraction was eluted with CH_2Cl_2 , which gave rubyrin **3** (107 mg, 24%).



R = Me, Et

Preparation of **Terpyrrole**

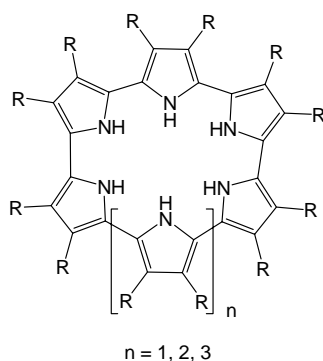
In a round-bottomed flask equipped with a condenser, the terpyrrole diester¹ was suspended in ethylene glycol followed by addition of 10 equivalents of sodium hydroxide. The mixture was degassed of oxygen by successive evacuation under vacuum for 5 minutes followed by purging with argon. The mixture was then heated to reflux for 2 hours after which time the mixture was cooled to ambient temperature followed by addition of water that had been bubbled with nitrogen. The precipitate that formed was then isolated by filtration. The material was then quickly purified by chromatography over silica gel using dichloromethane as the eluent to yield the terpyrrole. Characterization data for the hexamethylterpyrrole may be found in the original report.² Hexaethylterpyrrole: ¹H NMR (400 MHz, CDCl₃): δ [ppm] 7.78 (s, 2H), 7.66 (s, 1H), 6.58 (s, 2H), 2.53 (m, 12H, CH₂CH₃), 1.28 (t, J = 7.8 Hz, 6H), 1.13 (2t, J = 7.8 Hz, CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ [ppm] 125.65, 123.44, 122.77, 121.43, 120.83, 114.02, 18.85, 18.44, 18.26, 16.76, 16.38, 14.56. HRMS (FAB) m/e calc'd for C₂₄H₃₅N₃: 365.2831, found 365.2827.



Preparation of **4**

In a round-bottomed flask equipped with an argon inlet and a magnetic stirrer, the hexamethyl terpyrrole was dissolved in dichloromethane. 3,5-Di-*tert*-butylbenzaldehyde was added followed by a catalytic amount of TFA. The resulting dark solution was stirred at room temperature for 4 hours. DDQ was then added and the solution stirred at ambient temperature for 1 hour. The solvent was removed with the aid of a rotary evaporator. The residue was taken up in chloroform and washed twice with 10 % NaOH. The organic layer was separated off and dried over Na₂SO₄. The solvent was removed *in vacuo* on a rotary

evaporator. The resulting solid was purified by chromatography over a pre-basified silica gel column using dichloromethane as the eluent. The first orange band off the column was washed twice with 1N HCl and dried over Na₂SO₄. It was then taken to dryness using a rotary evaporator to afford the dihydrochloric salt of amethyrin. Characterization data for this compound may be found in the original report.³



Preparation of **5**, **6**, and **7** (n = 1,2, and 3)

A 1 L round bottom flask was charged with a stir bar, 500 mL of dichloromethane, and a solution of FeCl₃•6H₂O (2.7 g, 10 mmol) in 1 M hydrochloric acid (100 mL). The resulting biphasic solution was stirred at 300 RPM, while 3,3',4,4'-tetraethylbipyrrole⁴ (244 mg; 1 mmol) dissolved in dichloromethane (50 mL) was added slowly *via* a syringe pump over a period of 12 hours, with the needle submerged into the organic phase. For this slow continuous addition, a Sage syringe pump (model M365) was used. After completion of the addition, the reaction mixture was stirred for 6 more hours. The organic phase was separated but was not dried. The solvent was then removed *in vacuo*. The resulting crude dark green product was purified via column chromatography on silica gel using dichloromethane containing 0.5% methanol as the eluent to yield a hazelnut brown band of cyclo[6]pyrrole **5**. Increasing the polarity of the solvent system to 2% methanol yielded a yellow brown band of cyclo[8]pyrrole **7**. Further increasing the polarity to 7.5% methanol in dichloromethane afforded a grass green band consisting of cyclo[7]pyrrole **6**. The solvent was removed *in vacuo* and the residues recrystallized from dichloromethane/hexanes to yield the corresponding bis hydrochloride salts of **5**, **6**, and **7** as dark microcrystalline powders. Characterization data for these compounds may be found in the original reports.⁵

1. Sessler, J. L.; Aguilar, A.; Sanchez-Garcia, D.; Seidel, D.; Kohler, T.; Arp, F.; Lynch, V. M. *Org. Lett.* **2005**, *7*, 1887.

2. Hannah, S.; Seidel, D.; Sessler, J. L.; Lynch, V. *Inorg. Chim. Acta.* **2001**, 317, 211.
3. Sessler, J. L.; Gordon, A. E. V.; Seidel, D.; Hannah, S.; Lynch, V.; Gordon, P. L.; Donohoe, R. J.; Tait, C. D.; Webster, D. *Inorg. Chim. Acta.* **2002**, 341, 54.
4. Sessler, J. L.; Hoehner, M. C. *Synlett* **1994**, 212.
5. Köhler, T.; Seidel, D.; Lynch, V.; Arp, F. O.; Ou, Z.; Kadish, K. M.; Sessler, J. L. *J. Am. Chem. Soc.* **2003**, 125, 6871.

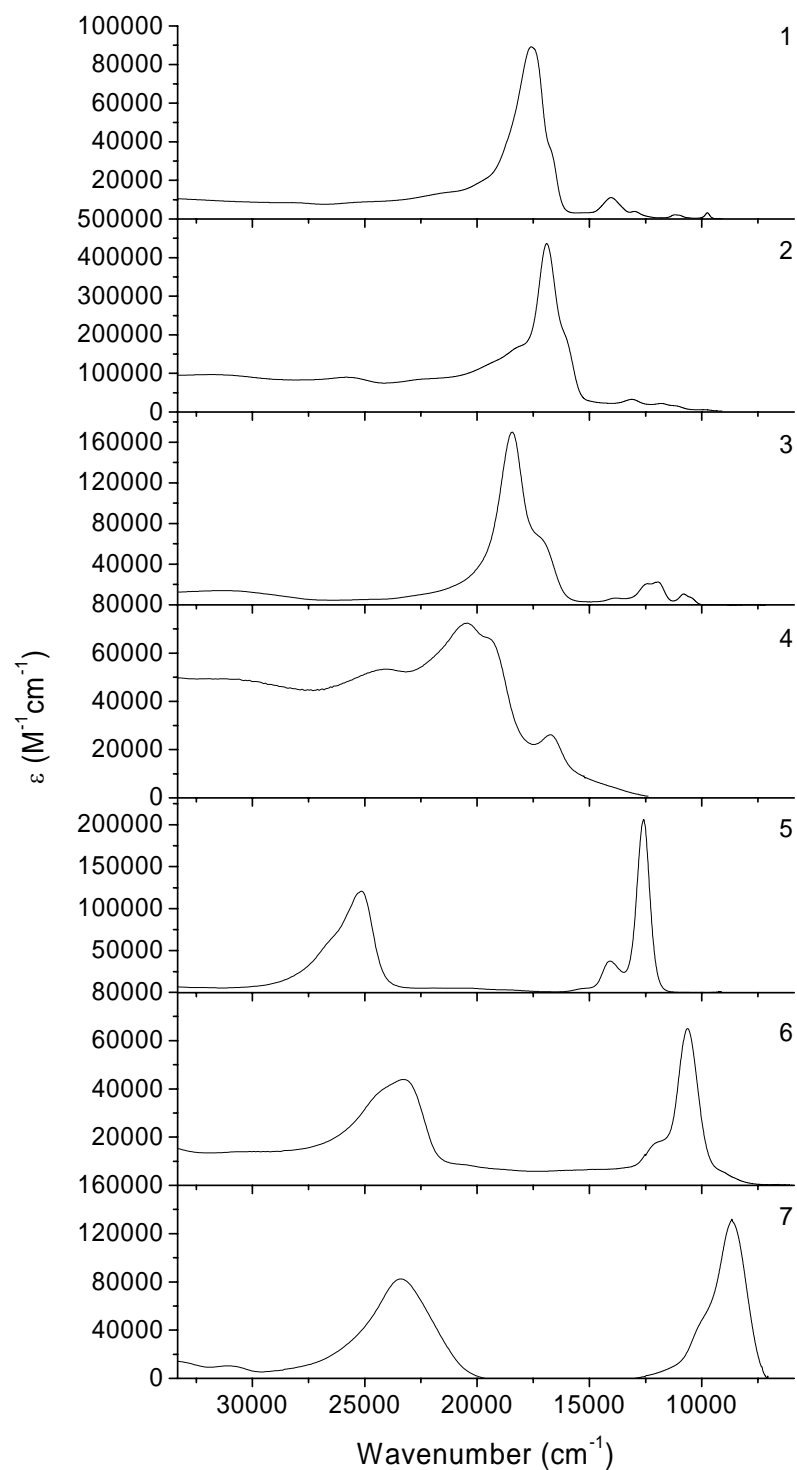


Figure S1. Steady-state absorption spectra of **1-7** in UV-VIS-NIR region. See references 6 - 9 in the text for the detailed extinction coefficients.

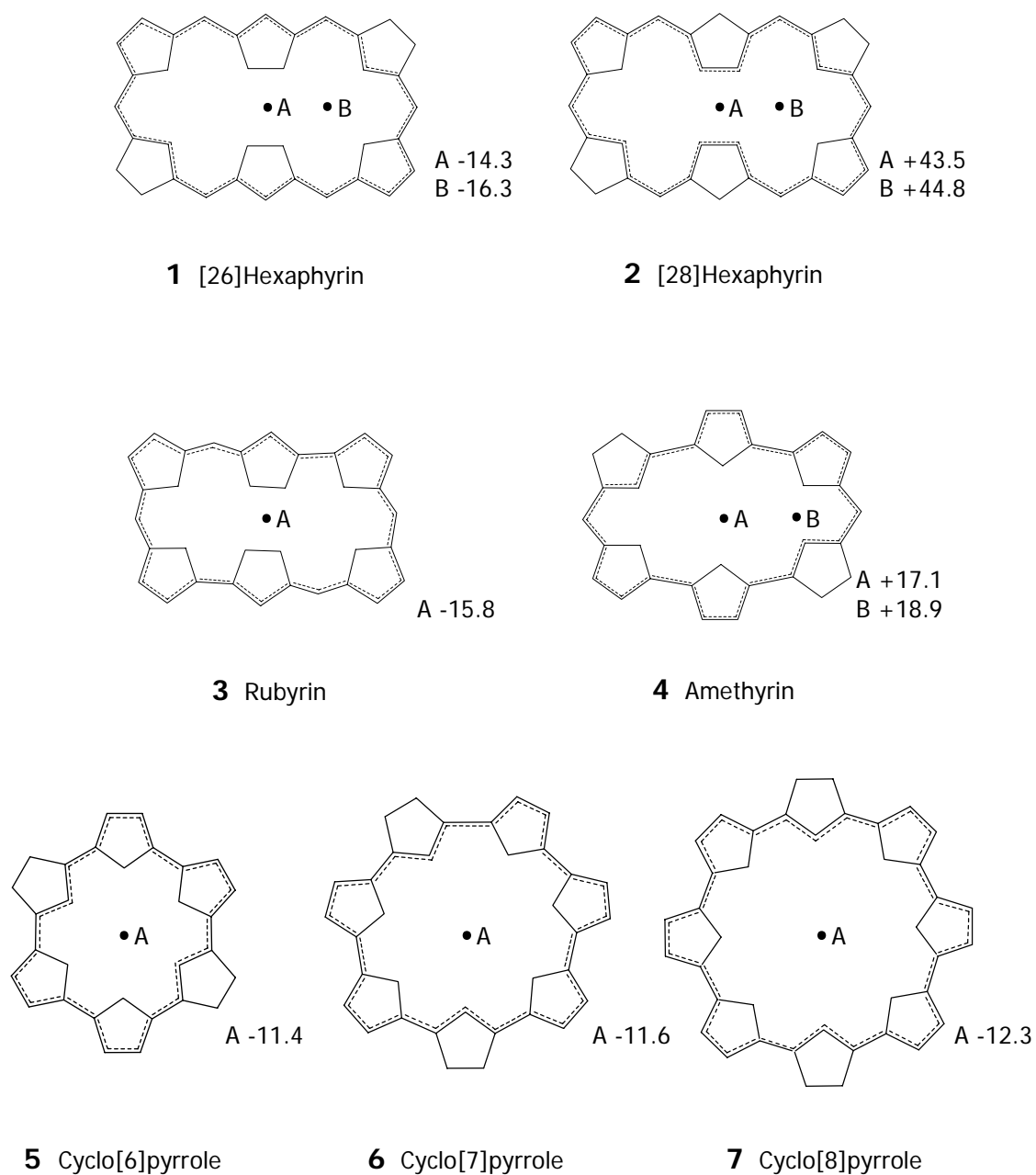


Figure S2. Schematic π -conjugation pathways (dotted lines) and NICS(0) values at the center of the rings for 1-7. β -Pyrrolic and meso substituents have been omitted for clarity.

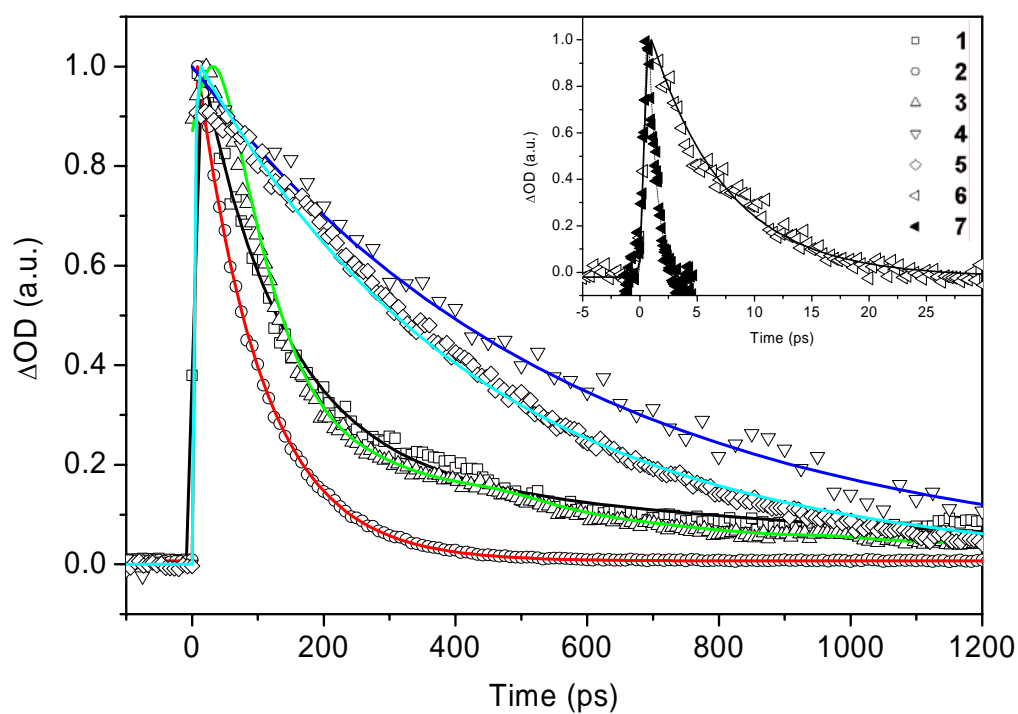


Figure S3. S₁-state decay profiles of **1-3** in toluene and **4-7** in CH₂Cl₂. The pump and probe wavelengths are indicated in Table 1, which correspond to the Q-like band excitation and the induced absorption maximum, respectively.

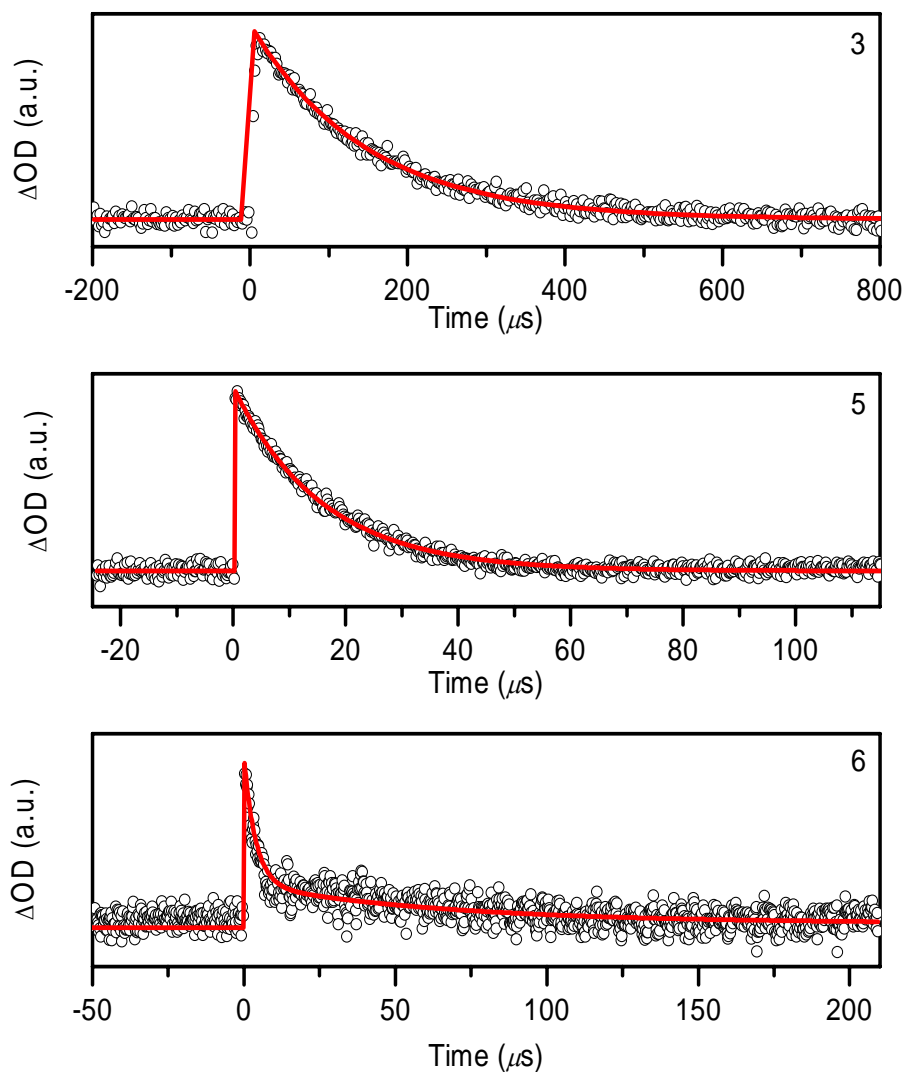


Figure S4. Nanosecond transient absorption decay profiles of **3** (top) in toluene and **5** (middle) and **6** (bottom) in CH_2Cl_2 . The pump and probe wavelengths are indicated in the footnotes of Table 1.

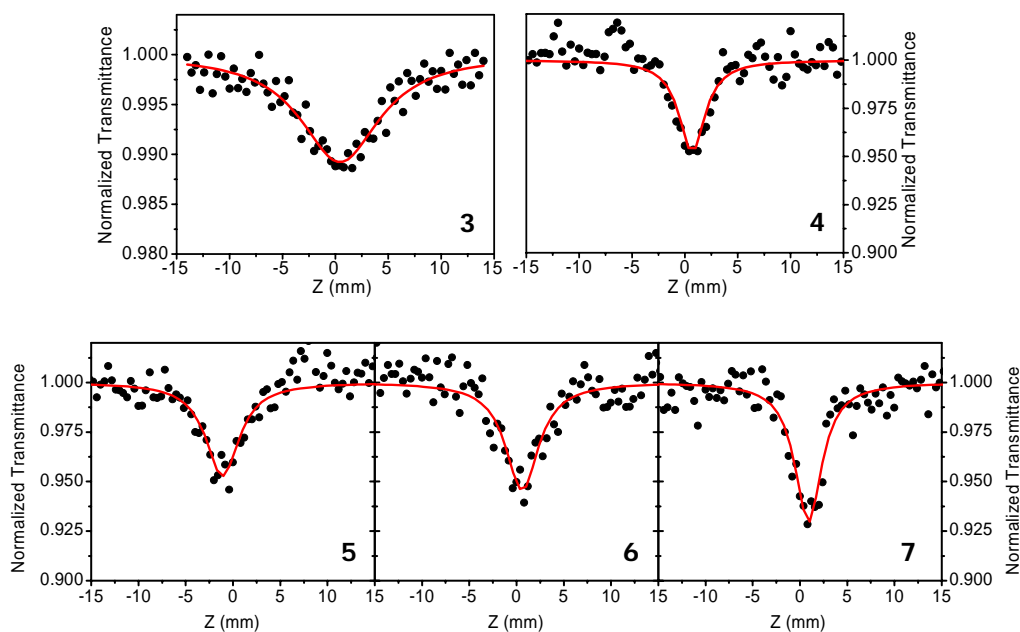


Figure S5. Open-aperture femtosecond Z-scan traces of **3** as measured in toluene and of **4-7** recorded in CH_2Cl_2 . The sample concentrations are 0.10 mM. The peak irradiance at the focal point is $80 \text{ GW}/\text{cm}^2$. The solid lines are the best-fit curves for the experimental data.