Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Photochemistry using Host-Guest Charge Transfer Paradigm: DMABN as a Dynamical Probe of Ground and Excited States

Rahul Gera and Jyotishman Dasgupta[†*]

[†]Department of Chemical Sciences, Tata Institute of Fundamental Research, Mumbai 400005, India.

*Email: dasgupta@tifr.res.in

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1. Materials and Methods:

Solvents and reagents were purchased from TCI Co., Ltd., S.D. Fine Chemicals and Sigma-Aldrich Co. D_2O was acquired from Sigma-Aldrich Co, Inc. and used as supplied for the reactions and NMR measurements.

NMR Measurements:

^1H and other 2D NMR spectra were recorded on Bruker (500 MHz, and 700 MHz) and Varian (600 MHz) spectrometer.

Steady State Absorption Measurements:

Absorption measurements were carried out in SPECORD 205 spectrophotometer. All the measurements were collected from 200-800 nm.

Transient Measurements:

Time-resolved transient measurements were carried out using an amplified laser source. 400 mW output from a mode-locked Ti:sapphire oscillator, MICRA-5, operating at 80 MHz repetition rate with a bandwidth of ~ 100 nm was amplified using a Coherent Legend Elite amplifier to provide a pulsed output of 4 W with spectral bandwidth of 65 nm and temporal bandwidth of 30 fs at 1 KHz repetition rate. The 4 mJ/pulse amplified output was split into two beams of equal power with help of a beam splitter. One portion is used for generation of a tunable output from an optical parametric amplifier (Coherent OPeraASolo). Other portion is used for generation of probe pulse, which is a white light continuum (~ 400 -1600 nm) generated using a 2 mm thick sapphire crystal. The optical parametric amplifier was used to generate 490 nm pump pulse which was attenuated to get an output of ~ 200-400 nJ per pulse that reaches the sample. The probe and the actinic pump pulses were focused, and overlapped temporally and spatially on the sample within a flow cuvette with 1 mm thickness. After passing through the sample, the probe photons were detected using a multichannel detector (Ultrafast Systems, Sarasota, Fl). Delay between pump and probe pulses were controlled using a motorized Newport translation stage that has a qudra-pass mirror assembly. 1 mm flow-cell with a 0.5 mm thick window was used for measurements. The flow rate was adjusted to replenish fresh sample and prevent photobleaching. NMR measurements were done pre- and post to the transient measurements to check the integrity of the host-guest complex. We detected no change of the samples after measurement. The samples in H_2O were prepared along with the samples in D_2O under identical conditions, and the measurements were performed under same settings to have a good comparison of the two datasets. The temporal instrument response is a Gaussian, with a FWHM of ~ 100 fs. The t = 0 between pump and probe pulses was assigned using cross-correlation and comparison to solvent response but, it was allowed to vary freely while fitting the kinetics. Fitting of

kinetics was done using a multi-exponential model convoluted with the IRF using home written codes in IGOR 5 Pro. Singular value decomposition (SVD) of the transient data was carried out by Surface Xplorer® software from Ultrafast Systems.

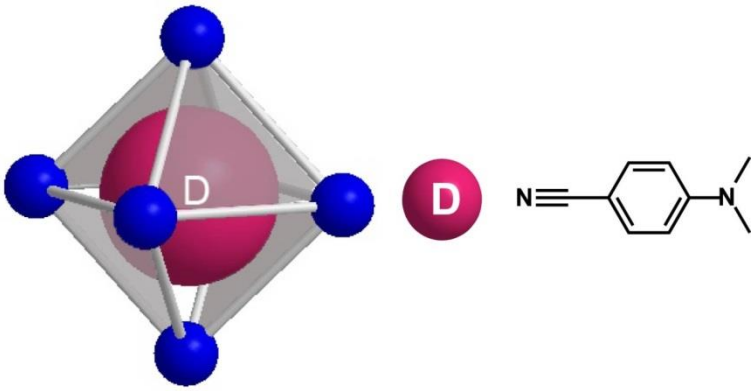
2. Synthesis of the cationic (Pd_6L_4) cage:

Cage preparation can be found M. Fujita *et al. Nature* 1995, 378, 469 and R. Gera *et al. J. Am. Chem. Soc.* 2014, 136, 15909. Protons of ethylenediamine are in the aliphatic region at δ 2.90 ppm. Reported values for proton Hα is δ 8.98 ppm as it is near to N ligated to Pd^{2+} thus downfield in comparison to Hβ (δ 8.48 ppm).

^{1}H – NMR of cage 1 (600MHz, D_2O, 298 K): δ 9.00 (d, pyridine-α), 8.51 (d, pyridine-β), 2.90 (s, Hc).

3. Synthesis of the inclusion complex DMABN ⊂ cage:

DMABN ⊂ cage inclusion complex was synthesized using the synthetic route reported by R. Gera *et al. J. Am. Chem. Soc.* **2014**, 136, 15909. Water insoluble DMABN solid (~ 19 mg) was stirred with a 5 ml solution of 2.5 mM cage 1 in D_2O for 1 h at room temperature. The colorless cage solution changes to orange. The solution was filtered through a 0.45 μ filter to remove the residual solid. Residual solid was removed by filtration using 0.45 micron filter. The host-guest complex in H_2O was synthesized simultaneously under identical conditions to avoid any ambiguity. The complex formation was confirmed by ^{1}H NMR and stability was tested before and after each spectroscopic measurement. ^{1}H–NMR of DMABN ⊂ Cage (500MHz, D_2O, 298 K): δ 9.27 (d, pyridine-α, Cage), 8.65 (d, pyridine-β, Cage), δ 5,24 (d, Ha, DMABN), δ 4.94 (d, Hb, DMABN), δ 2.94 (s, Hc, Cage), δ 1.40 (s, Me, DMABN); [Inset DMABN free in solution, (600 MHz, CDCl3, 298 K): δ 7.46 (d, Ha, DMABN), δ 6.64 (d, Hb, DMABN), δ 3.03 (s, Me, DMABN)].



4. **Structural Information from NMR: Through Space proton-proton distances**

These measurements were carried out on 700 MHz BRUKER NMR spectrometer at room temperature.

A proton pairs (I and S) give rise to NOE intensity when present close in space (~ 4 – 5 Å), for a given mixing time. NOE intensity is proportional to the I-S cross relaxation rate (σ_{IS})

η_{IS} = intensity of the NOE between I and S, τ_m is experimental mixing time.

$$\eta_{IS} = \sigma_{IS}\tau_m$$

Cross relaxation rate is proportional to the internuclear distances (r_{IS}^{-6}) described by

$$\sigma_{IS} = kr_{IS}^{-6}$$

Here,

$$k = \left(\frac{\mu_\circ}{4\pi}\right)\frac{\hbar^2\gamma^4}{10}\left(\frac{6\tau_c}{1+4\omega^2\tau_c^2} - \tau_c\right)$$

μ_0,γ, and ω is equivalent for a given experiment.

Selective saturation of a spin in a given transient 1D-NOESY spectrum would reflect in change of intensities of protons correlated to it in spatial proximity. Difference spectrum of an off-resonance spectrum with an on resonance saturation spectrum, will provide the information about protons correlated to each other in space. Assuming k is also constant, and then the ratio of the intensities of a pair of NOE signals η_{IS}: η_{I2S} within that spectrum can be proportional to their ratio of internuclear distances and this ratio will be independent of mixing time.

$$\frac{\eta_{I1S}}{\eta_{I2S}} = \frac{r_{I1S}^{-6}}{r_{I2S}^{-6}} \qquad \cdots (1)$$

Distances were calculated using the nondispersive features in NOE difference spectrums.

Distance calculation between Hb and Me - difference NOE spectrum of DMABN ⊂ Cage

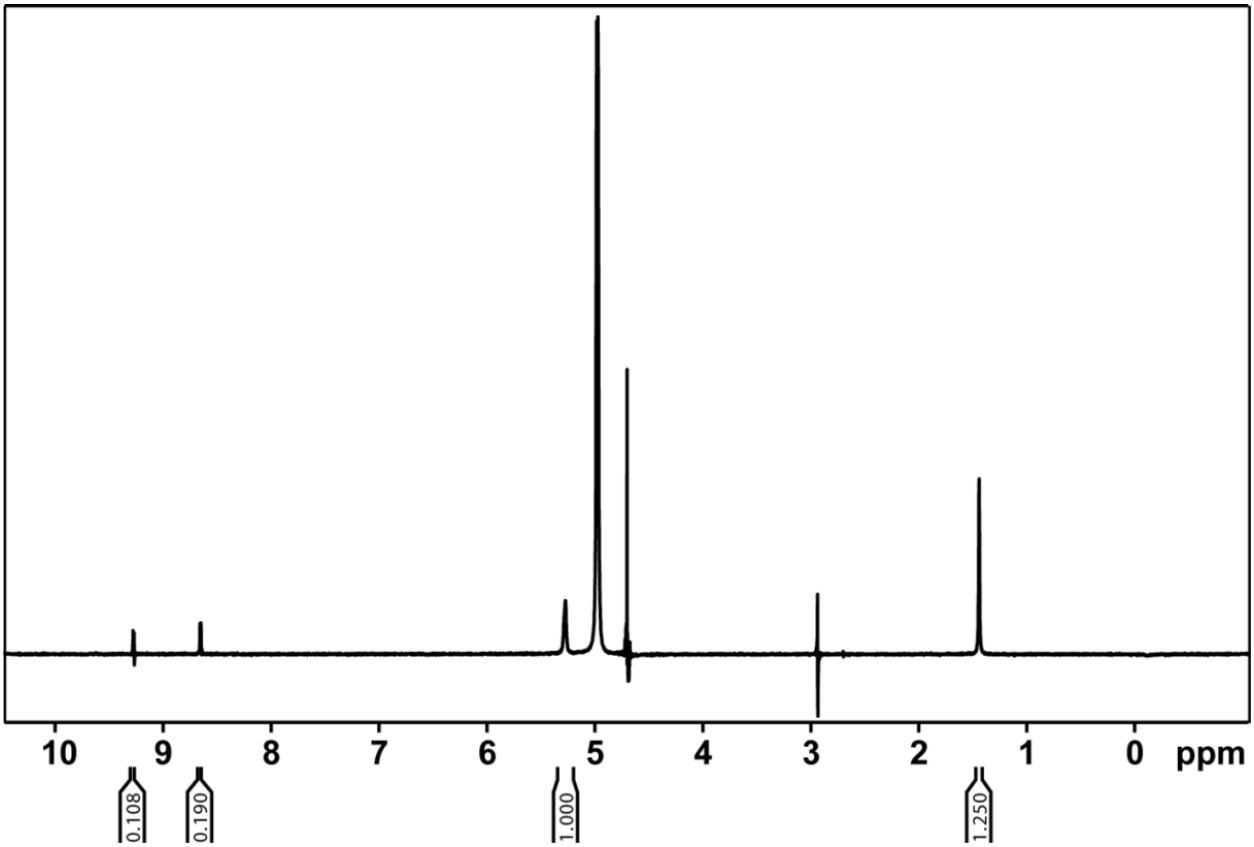
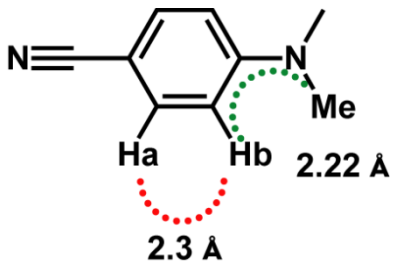


Figure S1. 1D- NOE difference spectrum for DMABN ⊂ cage obtained by saturating proton Hb of DMABN

Here, I = Hb, 1S =Ha, 2S = Me, η_{HbHa}= 1, η_{HbMe}= 1.25, r_{HbHa}= 2.3 Å

$$\frac{\eta_{I1S}}{\eta_{I2S}} = \frac{r_{I1S}^{-6}}{r_{I2S}^{-6}} \Rightarrow \frac{\eta_{HbHa}}{\eta_{HbMe}} = \frac{r_{HbHa}^{-6}}{r_{HbMe}^{-6}} == \frac{1}{1.25} = \frac{2.3^{-6}}{r_{HbMe}^{-6}} \Rightarrow r_{HbMe} = 2.22 \text{ Å}$$



Distance calculation between Ha and Me - difference NOE spectrum of DMABN ⊂ Cage

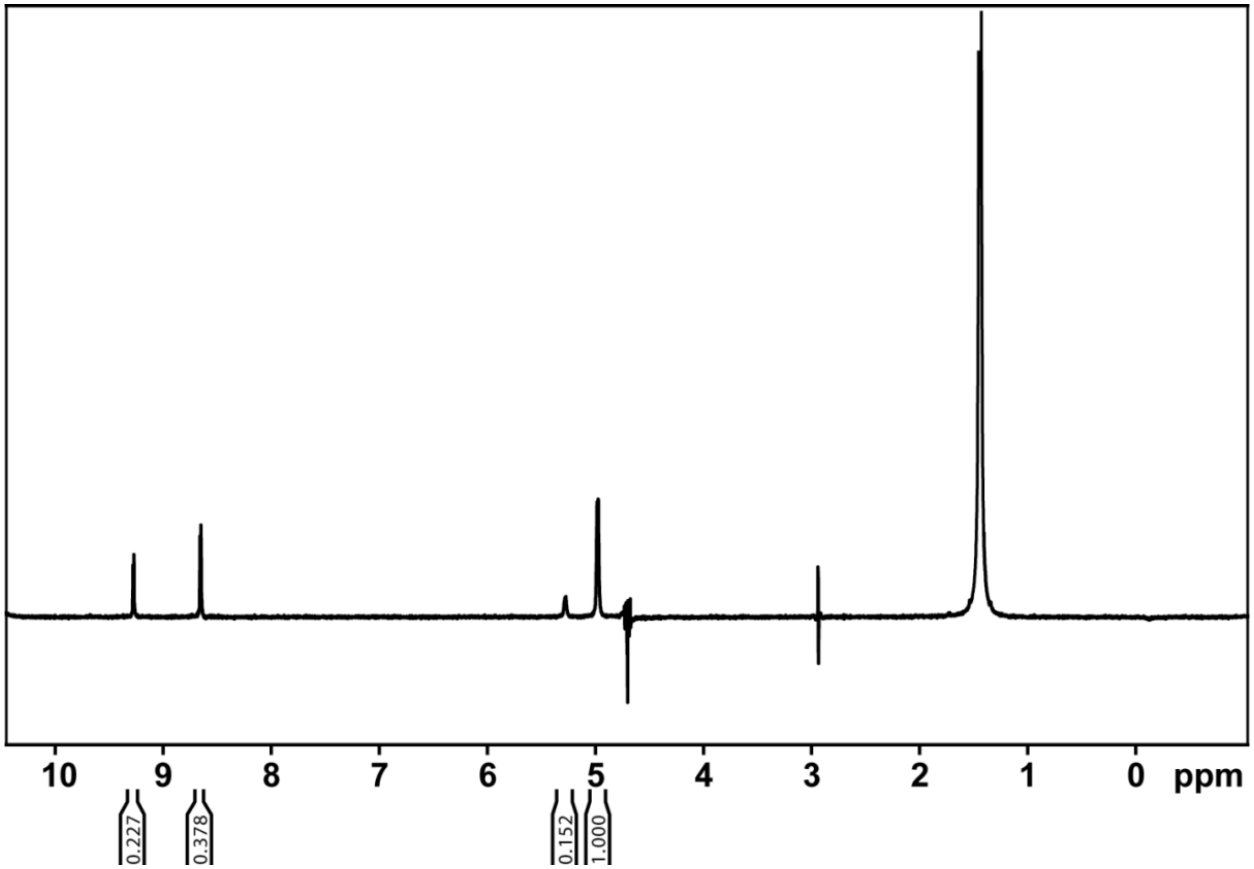
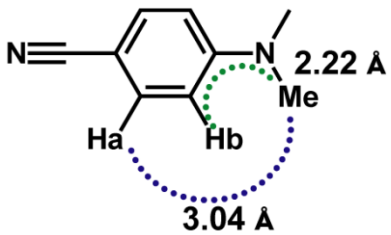


Figure S2. 1D- NOE difference spectrum for DMABN ⊂ cage obtained by saturating proton Me of DMABN

I = Me, 1S =Hb, 2S = Ha, η_{MeHb}= 1, η_{MeHa}= 0.152, r_{MeHb}= 2.22 Å

$$\frac{\eta_{MeHb}}{\eta_{MeHa}} = \frac{r_{MeHb}^{-6}}{r_{MeHa}^{-6}} == \frac{1}{0.152} = \frac{2.22^{-6}}{r_{MeHa}^{-6}} \Rightarrow r_{MeHa} = 3.04 \text{ Å}$$



Distance calculation between Hβ and Me - difference NOE spectrum of DMABN ⊂ Cage

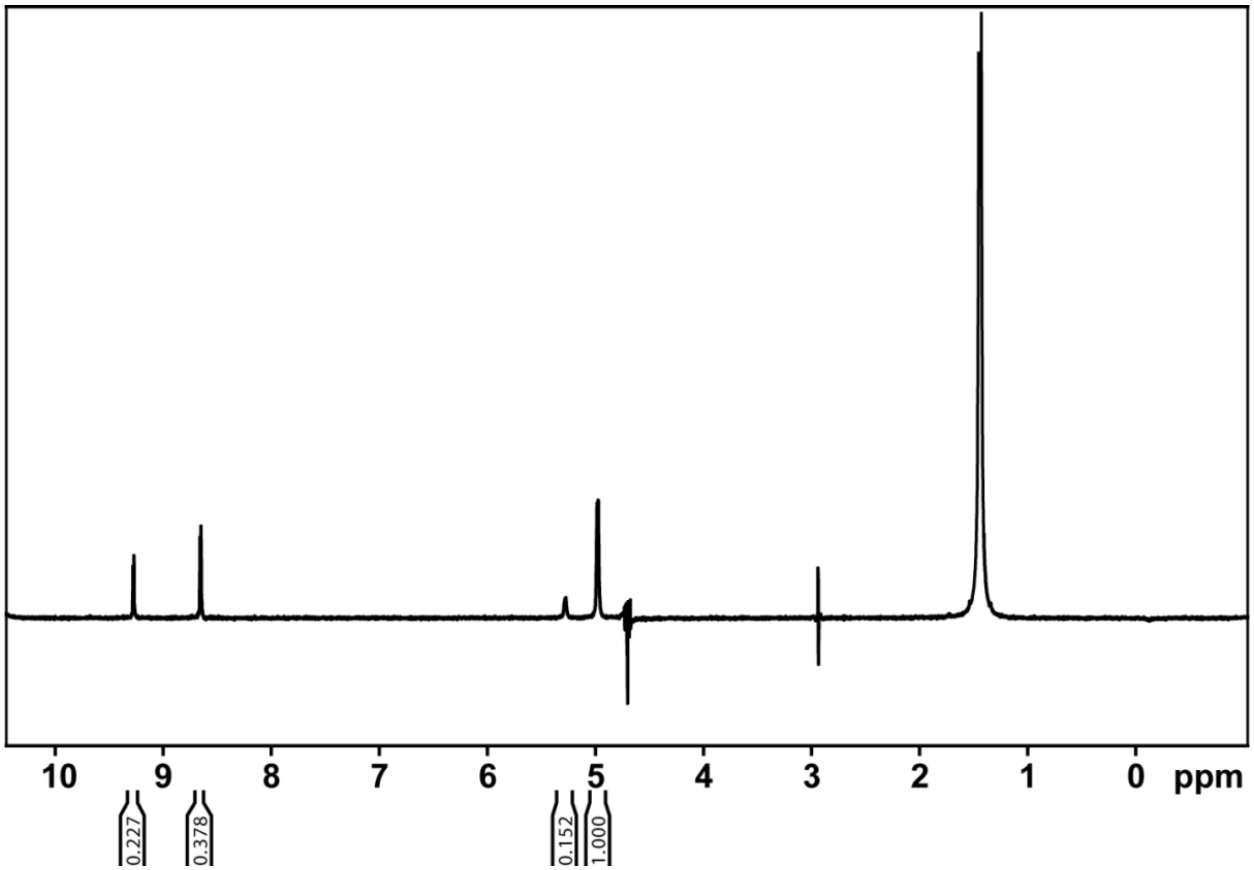
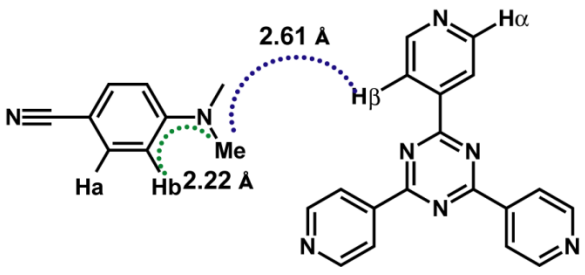


Figure S3. 1D- NOE difference spectrum for DMABN ⊂ cage obtained by saturating proton Me of DMABN

I = Me, 1S =Hb, 2S = Hβ, η_{MeHb}= 1, $\eta_{MeH\beta}$= 0.378, r_{MeHb}= 2.22 Å

$$\frac{\eta_{MeHb}}{\eta_{MeH\beta}} = \frac{r_{MeHb}^{-6}}{r_{MeH\beta}^{-6}} == \frac{1}{0.378} = \frac{2.22^{-6}}{r_{MeH\beta}^{-6}}$$

$$r_{MeH\beta} = 2.61 \text{ Å}$$



Distance calculation between Hα and Me - difference NOE spectrum of DMABN ⊂ Cage

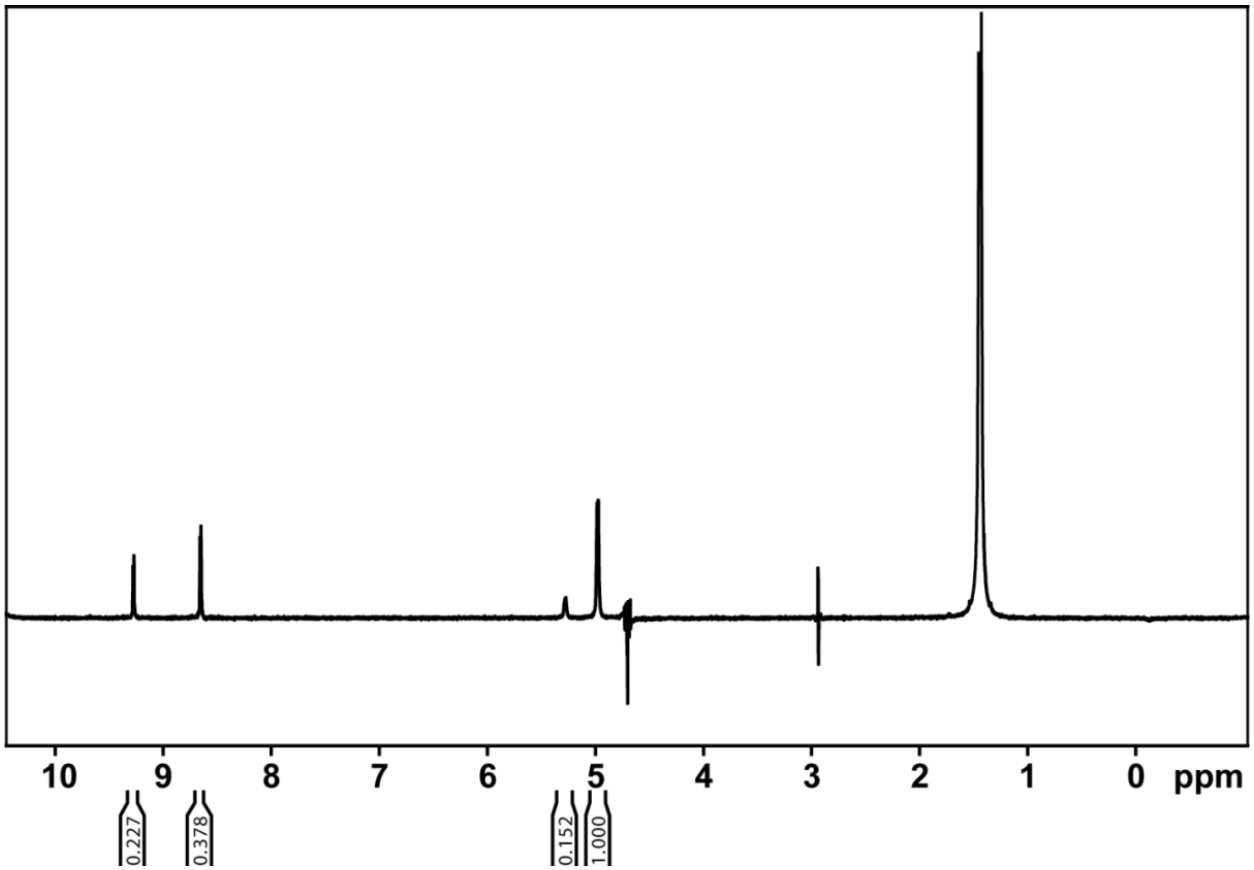
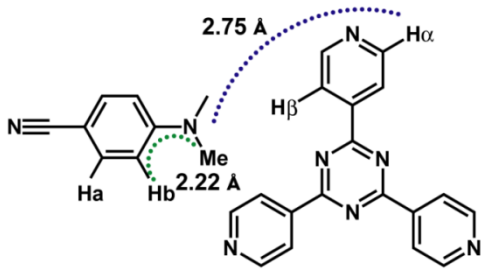


Figure S4. 1D- NOE difference spectrum for DMABN ⊂ cage obtained by saturating proton Me of DMABN

I = Me, 1S =Hb, 2S = Hα, η_{MeHb}= 1, $\eta_{MeH\alpha}$= 0.378, r_{MeHb}= 2.22 Å

$$\frac{\eta_{MeHb}}{\eta_{MeH\beta}} = \frac{r_{MeHb}^{-6}}{r_{MeH\alpha}^{-6}} == \frac{1}{0.227} = \frac{2.22^{-6}}{r_{MeH\alpha}^{-6}}$$

$$r_{MeH\alpha} = 2.75 \text{ Å}$$



Pair of protons	Spatial distances (Å)
Hb (DMABN) - Me (DMABN)	2.20
Ha (DMABN) – Me (DMABN)	3.04
Me (DMABN) – Hα (Cage)	2.75
Me (DMABN) – Hβ (Cage)	2.61

Table ST1. Calculated distances between ^{1}H close in space using NOE difference spectroscopy

5. Time-evolution of the broad Visible excited state absorption signal

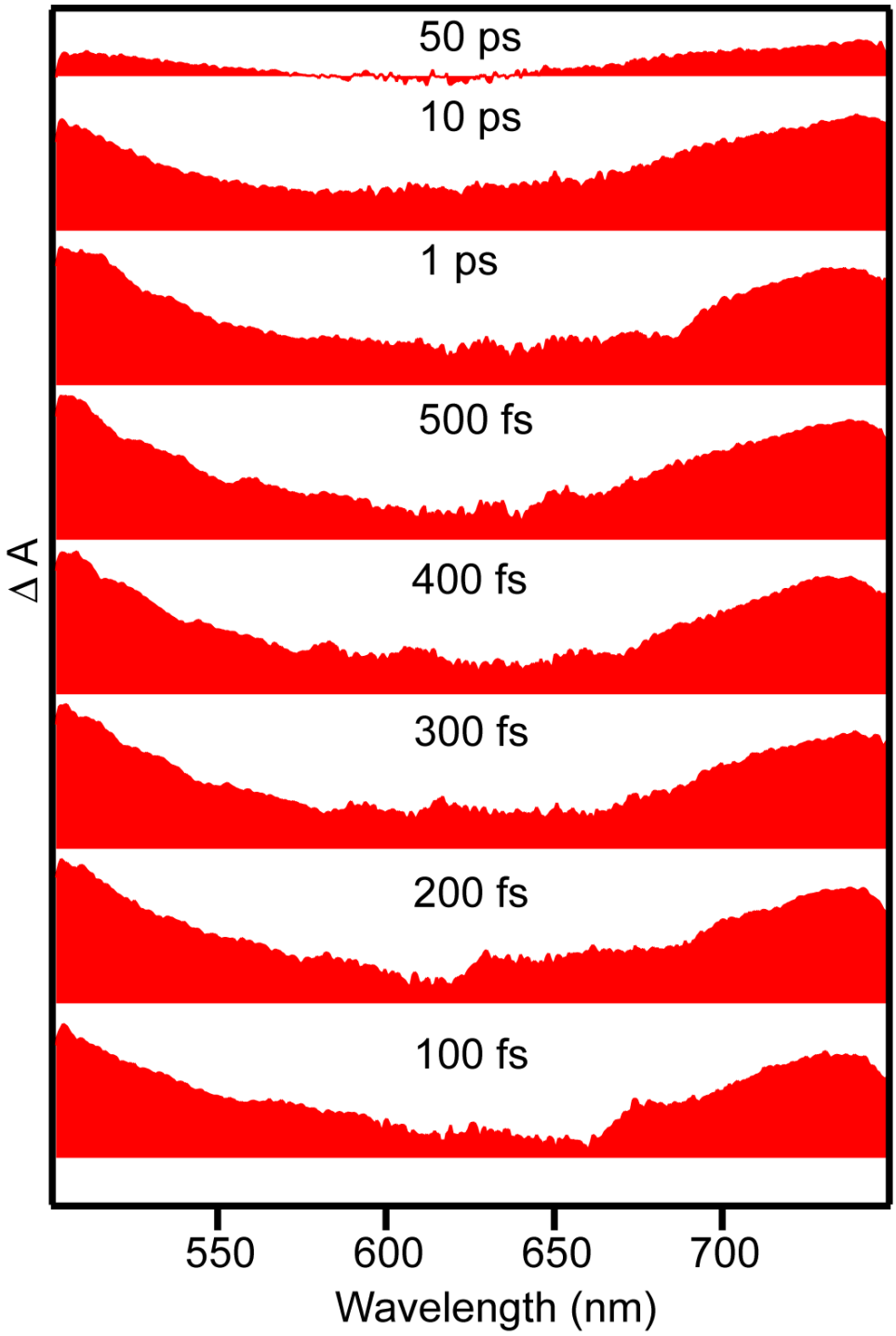


Figure S5. Time-evolution of the broad NIR excited state absorption signal in DMABN ⊂ Cage after excitation with λ_{pump} = 490 nm.

6. Kinetics of excited state absorption signal in Visible

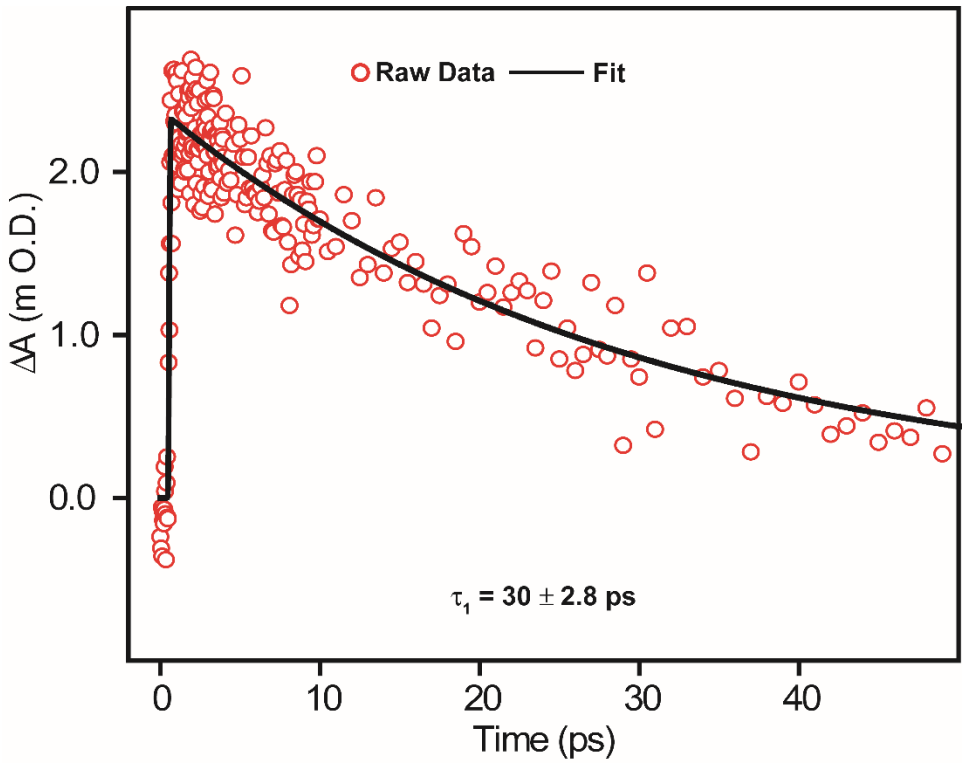


Figure S6. Kinetics of excited state absorption signal for DMABN ⊂ Cage at 545 nm after excitation with λ_{pump} = 490 nm.

7. Time-evolution of the broad NIR excited state absorption signal

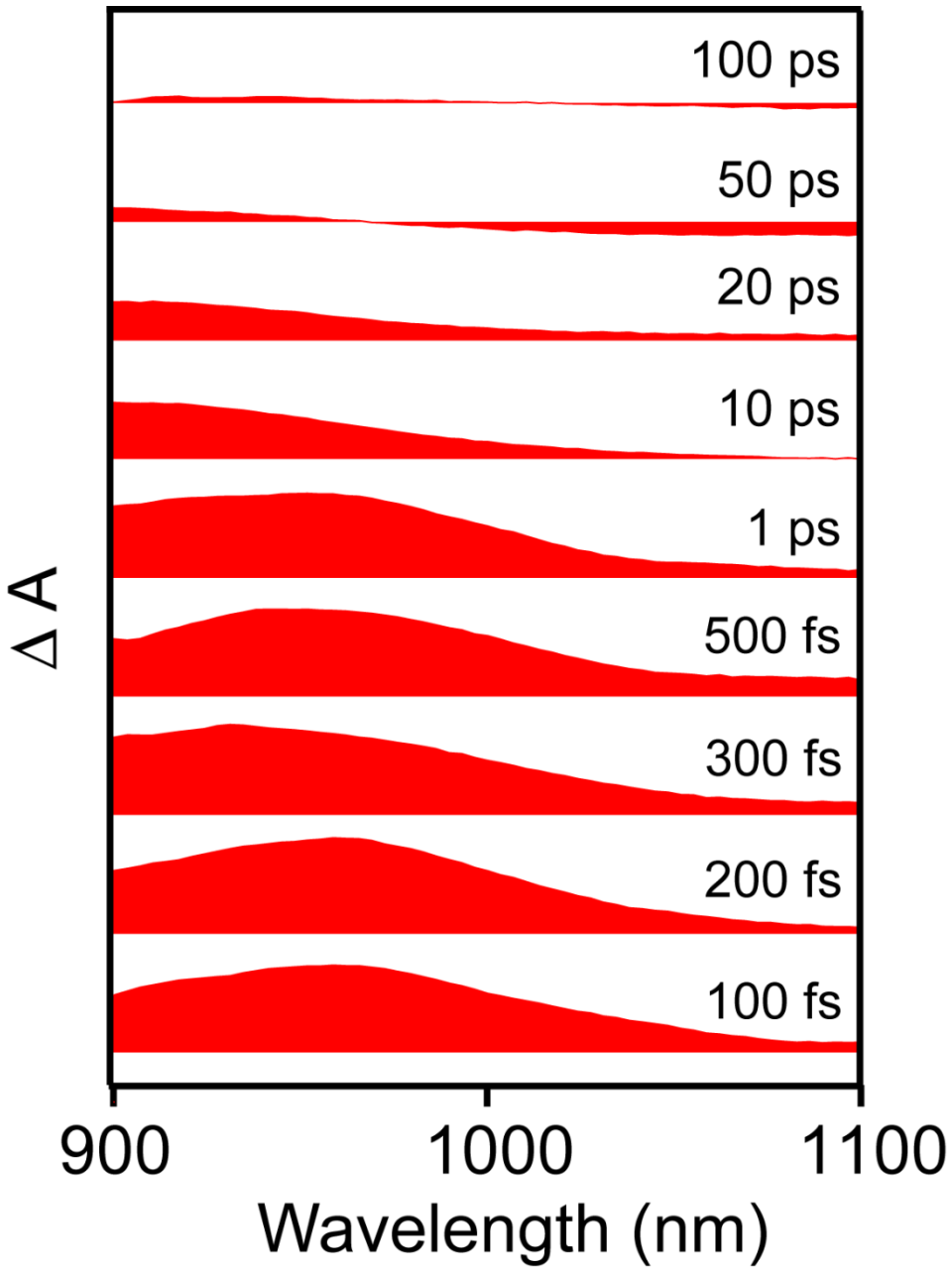


Figure S7. Time-evolution of the broad NIR excited state absorption signal in DMABN ⊂ Cage after excitation with λ_{pump} = 490 nm.

8. Kinetics of excited state absorption signal in NIR

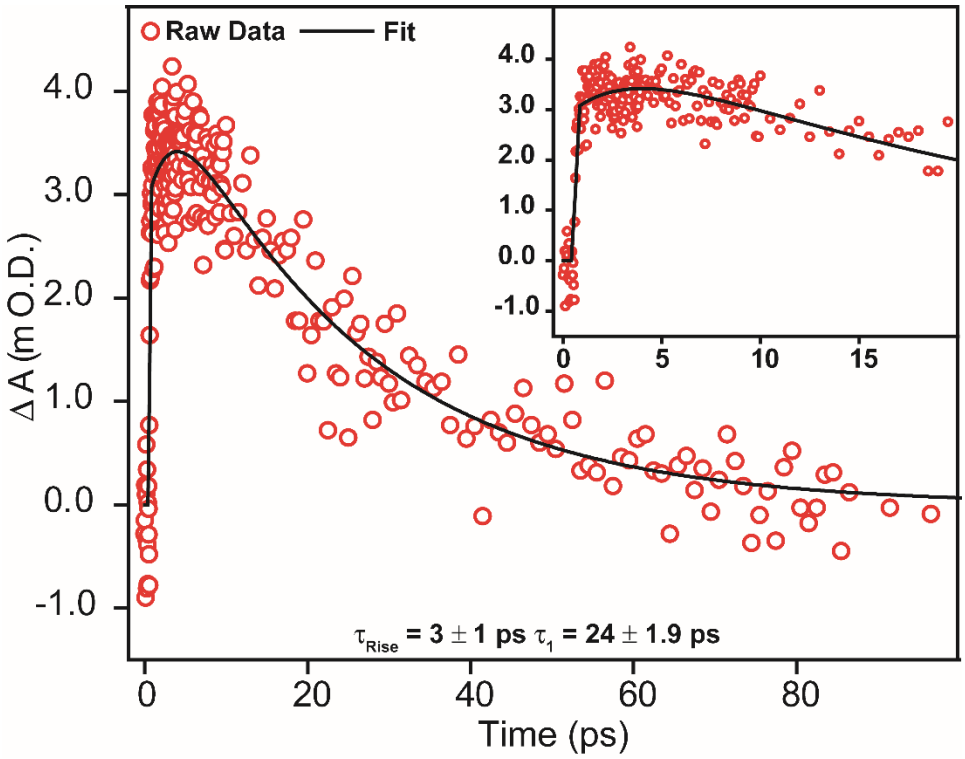


Figure S8. Kinetics of excited state absorption signal for DMABN ⊂ Cage at 880 nm after excitation with λ_{pump} = 490 nm.

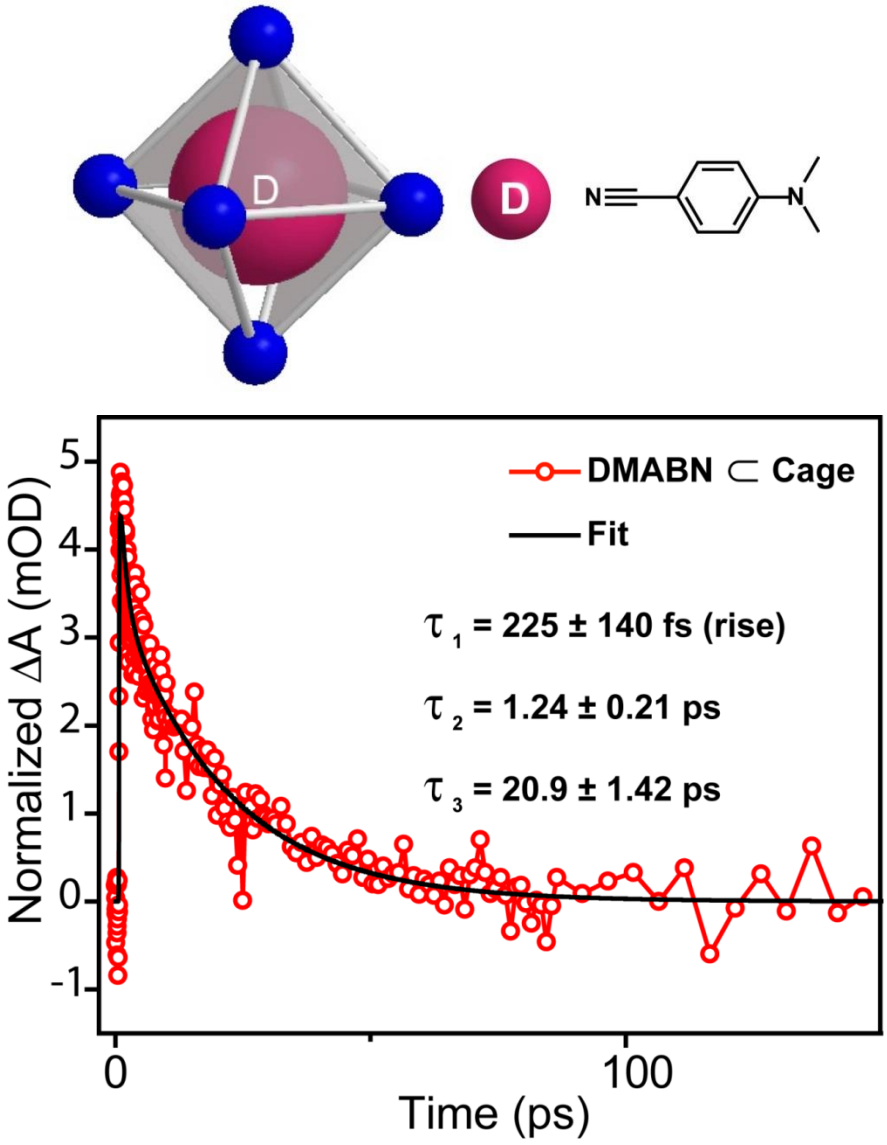


Figure S9. Kinetics of excited state absorption feature at 952 nm for DMABN ⊂ cage after excitation with 490 nm pump pulse. This data is also included the published manuscript **R. Gera *et al. J. Am. Chem. Soc.* 2014, 136, 15909.**