Electronic Supporting Supplementary

for

Photophysical Properties and Singlet Oxygen Generation of *Meso*-Iodinated Free-Base Corroles

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MS, ^{1}H-NMR and ^{19}F-NMR data was utilized for the primary conformation of corroles **1**, **2** and **3**.

(a)10-(2-hydroxylphenyl)-5,15-bis(pentafluorophenyl)corrole:　^{1}H-NMR　(CDCl$_3$,　400MHz): δppm: 7.31 (2H, m, Ph-H), 7.68 (1H, m, Ph-H), 7.88 (1H, q, Ph-H), 8.56 (2H, d, pyrrole-H), 8.69 (4H, q, pyrrole-H), 9.10 (2H, d, pyrrole-H). 19F-NMR (CDCl3, 376MHz): δppm: -137.3 (4F, m), -152.9 (2F, m), -161.9 (4H, m). HR-MS: calcd exact mass(C$_{37}$H$_{17}$F$_{10}$N$_4$O): 722.6502[M+H$^+$]. Found: 722.6813.

(b)10-(2-hydroxyl-5-iodophenyl)-5,15-bis(pentafluorophenyl)corrole:　^{1}H-NMR　(CDCl$_3$, 400MHz): δppm: 7.11(1H, d, Ph-H), 7.96 (1H, 2d, Ph-H), 8.22 (1H, d, Ph-H), 8.58 (2H, d, pyrrole-H), 8.66 (2H, d, pyrrole-H), 8.73 (2H, d, pyrrole-H), 9.12 (2H, d, pyrrole-H). 19F-NMR (CDCl3, 376MHz): δppm: -138.3 (4F, d), -152.6 (2F, t), -161.8 (4F, m). HR-MS: calcd exact mass(C$_{37}$H$_{16}$F$_{10}$IN$_4$O): 849.0209[M+H$^+$]. Found: 849.0850.

(c)10-(2-hydroxyl-3,5-bisiodophenyl)-5,15bis(pentafluorophenyl)corrole:　^{1}H-NMR　(CDCl$_3$, 400MHz): δppm: 7.67(1H, d, Ph-H), 8.20(1H, s, Ph-H), 8.44(2H, d, pyrrole-H), 8.59(2H, d, pyrrole-H), 8.77(2H, d, pyrrole-H), 9.04(2H, s, pyrrole-H).^{19}F-NMR (CDCl$_3$, 376MHz): δppm: -137.54(4F, m), -151.97(2F, s), -161.25(4F, s). HR-MS: calcd exact mass(C$_{37}$H$_{15}$F$_{10}$I$_2$N$_4$O): 974.9170[M+H$^+$]. Found: 974.9174.

Because sample **3** is newly synthesized, the preparation procedure is described as follows: a dichloromethane solution (100 mL) charged with 0.8 mmoL 5-(pentafluorophenyl)dipyrromethane was stirred for 5 min. 0.4 mmoL 3,5-diiodosalicylaldehyde and 20 µL TFA (trifluoroacetic acid) were added into this solution and reacted for 5 h in the room temperature. 40 µL Et3N (3 subindex) and 1 mmol DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) was injected into the reaction mixture and stirred for another hour at the room temperature. The crude product was obtained from the black reaction mixture via flash chromatography with dichloromethane. After collecting the weak fluorescent product, a second chromatography was developed with a solvent mixture (dichloromethane/hexane, 1:3) to obtain the pure green product with 5% isolated yield. The high-resolution mass spectrum of **3** is shown in the ESI2(High-resolution mass spectrum of **3**).pdf file.

Table S1. Molar Absorption Coefficient of Three Investigated Corroles.

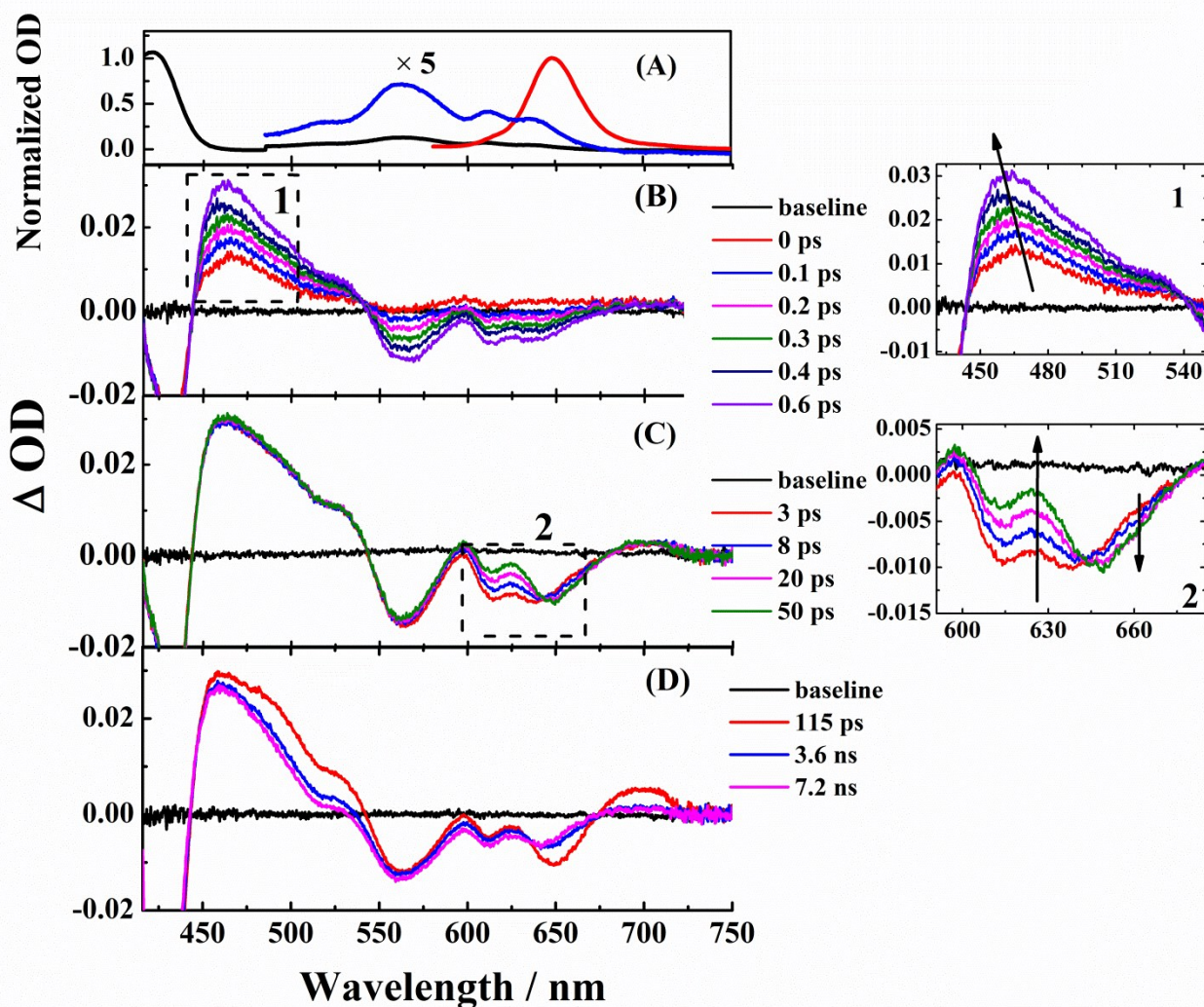| compd	Soret band $\varepsilon(10^5\,M^{-1}cm^{-1})$	Q bands $\varepsilon(10^5\,M^{-1}cm^{-1})$			
	421 nm	514 nm	564 nm	611 nm	637 nm
1	1.12	0.07	0.15	0.09	0.08
2	1.01	0.08	0.15	0.09	0.07
3	0.84	0.06	0.14	0.08	0.06

Figure S1. Transient absorption spectra of **Corrole 1** in benzene. The pump wavelength was 400 nm (90-100 fs). (left panel) (A) Normalized ground-state absorption (black for Soret band and blue for the enlarged Q bands) and steady-state fluorescence (red) in benzene. (B) The transient spectra from 0 ps to 0.6 ps**,** (C) 3 ps to 50 ps, and (D) 115 ps to 7.2 ns. (right panel) the zoom of region 1 and region 2.
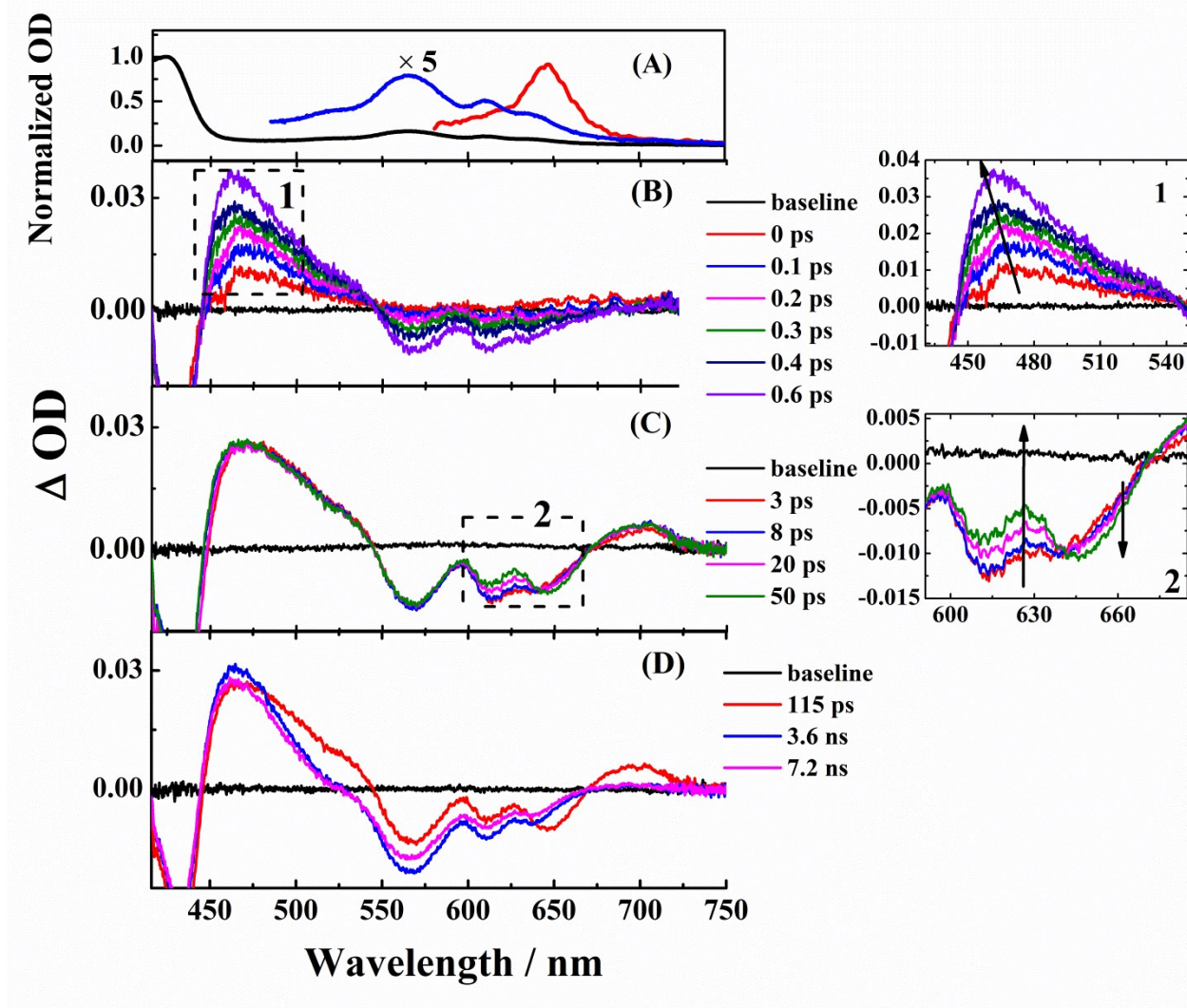
Figure S2. Transient absorption spectra of Corrole **3** in benzene. The pump wavelength was 400 nm (90-100 fs). (left panel) (A) Normalized ground-state absorption (black for Soret band and blue for the enlarged Q bands) and steady-state fluorescence (red) in benzene. (B) The transient spectra from 0 ps to 0.6 ps, (C) 3 ps to 50 ps, and (D) 115 ps to 7.2 ns. (right panel) the zoom of region 1 and region 2.
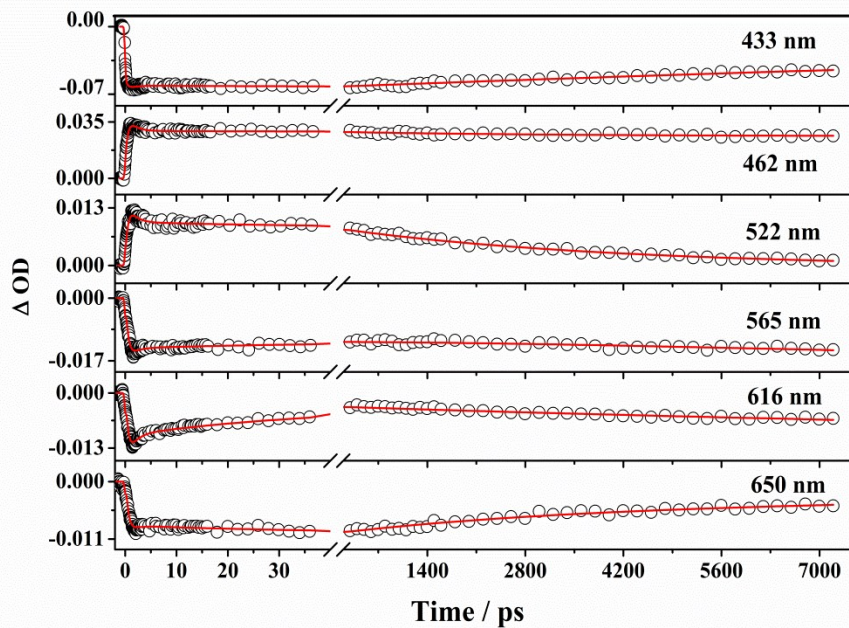
Figure S3. Time profiles at several selected wavelengths of Corrole **1** in benzene after 400 nm (90-100 fs) pump. Red solid lines are the fitting results obtained from global target analysis.
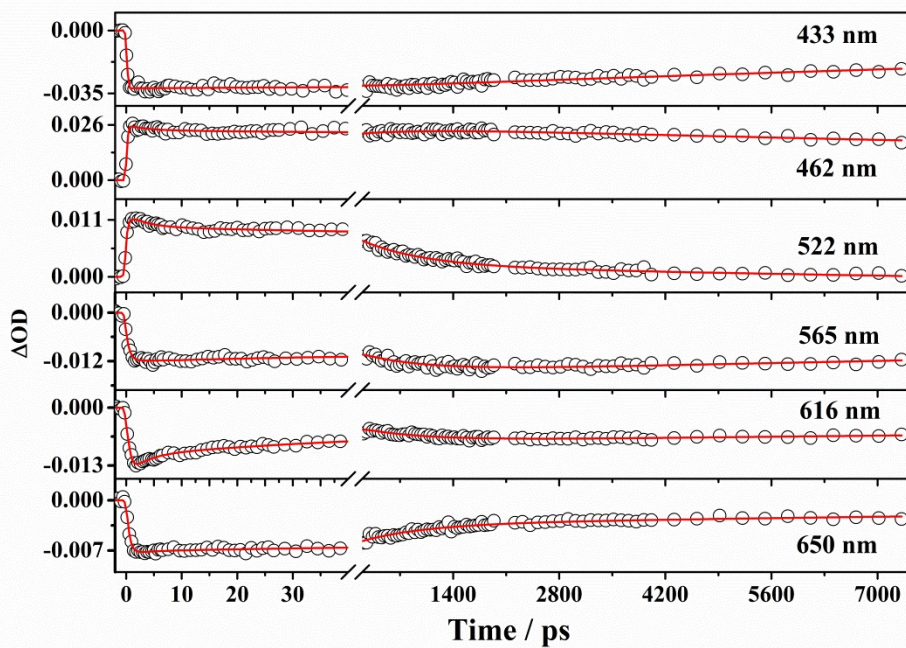

Figure S4. Time profiles at several selected wavelengths of Corrole **3** in benzene after 400 nm (90-100 fs) pump. Red solid lines are the fitting results obtained from global target analysis.
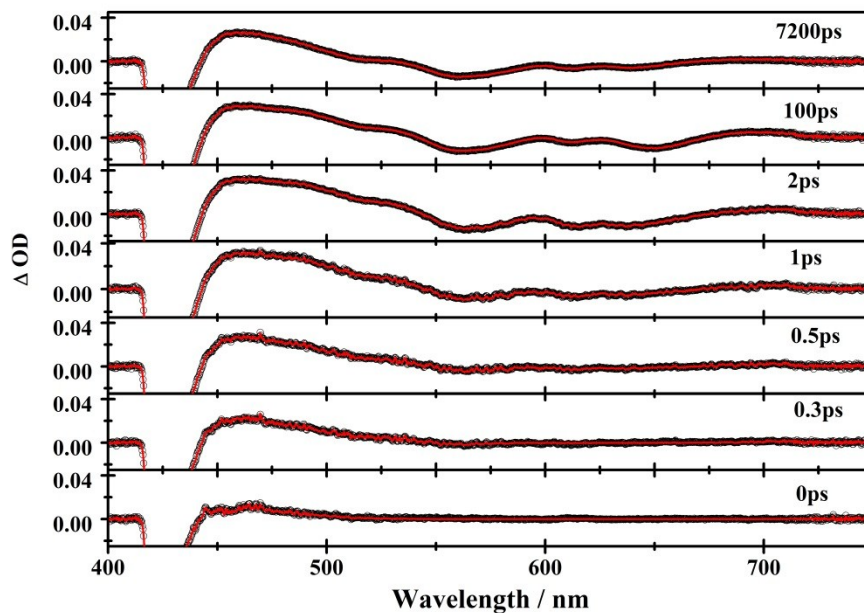
Figure S5. Transient absorption spectra at different times of Corrole **1**; solid red lines are results of global target analysis.
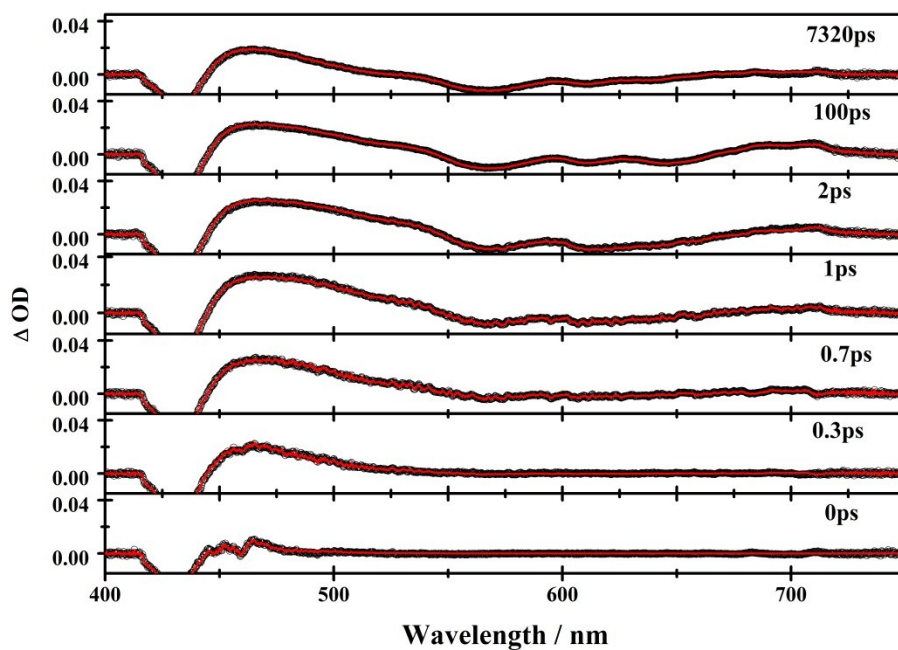

Figure S6. Transient absorption spectra at different times of Corrole **3**; solid red lines are results of global target analysis.
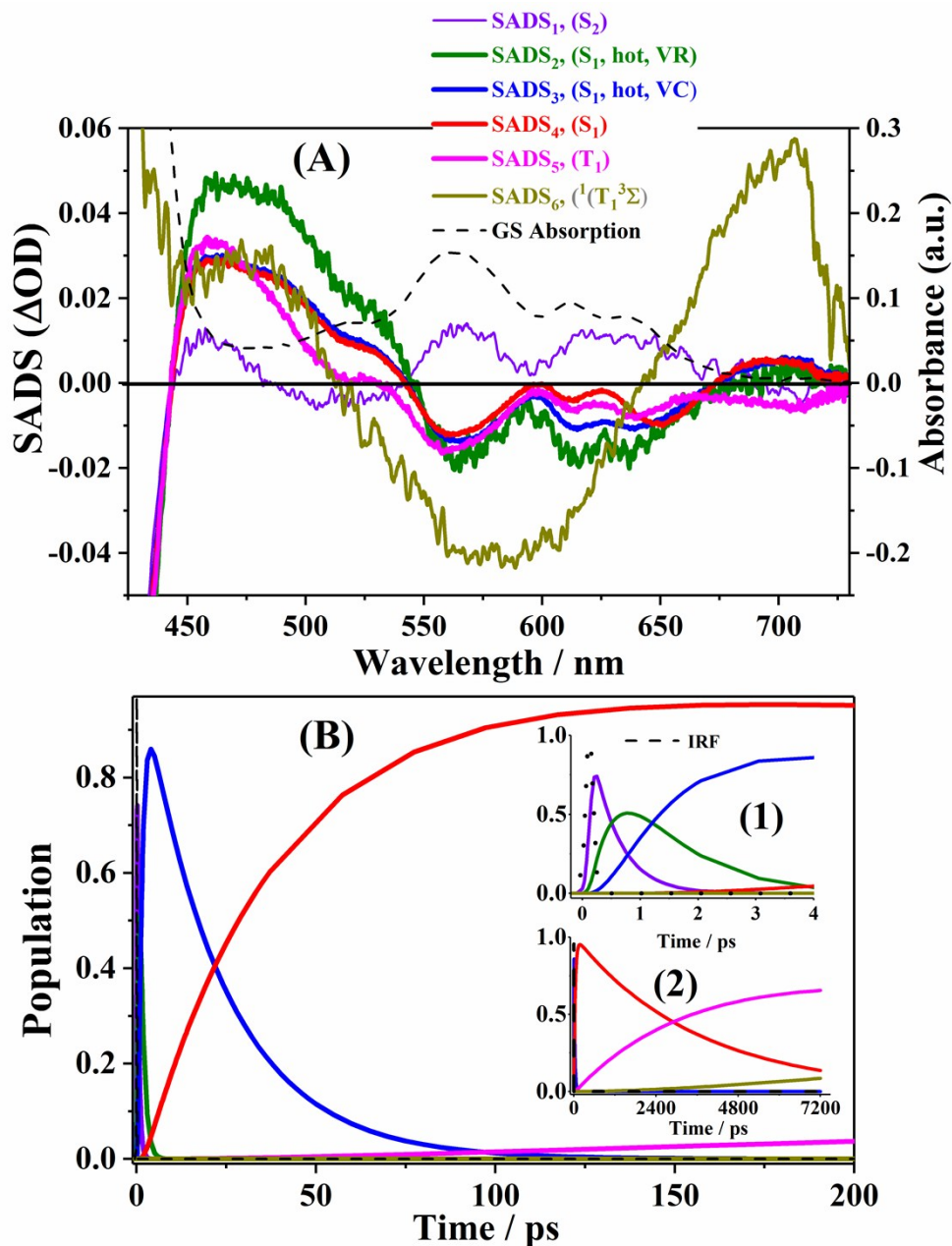
Figure S7. (A) Species associated spectra(SADS) obtained from target analysis of TA data for Corrole **1** in benzene after Soret excitation. (B) The population profiles of the different species in 200 ps time window, enlarge view of population profiles in 4 ps time window (inset 1) and 7200 ps (inset 2).

Figure S8. (A) Species associated spectra(SADS) obtained from target analysis of TA data for Corrole **3** in benzene after Soret excitation. (B) The population profiles of the different species in 200 ps time window, enlarge view of population profiles in 4 ps time window (inset 1) and 7200 ps (inset 2).
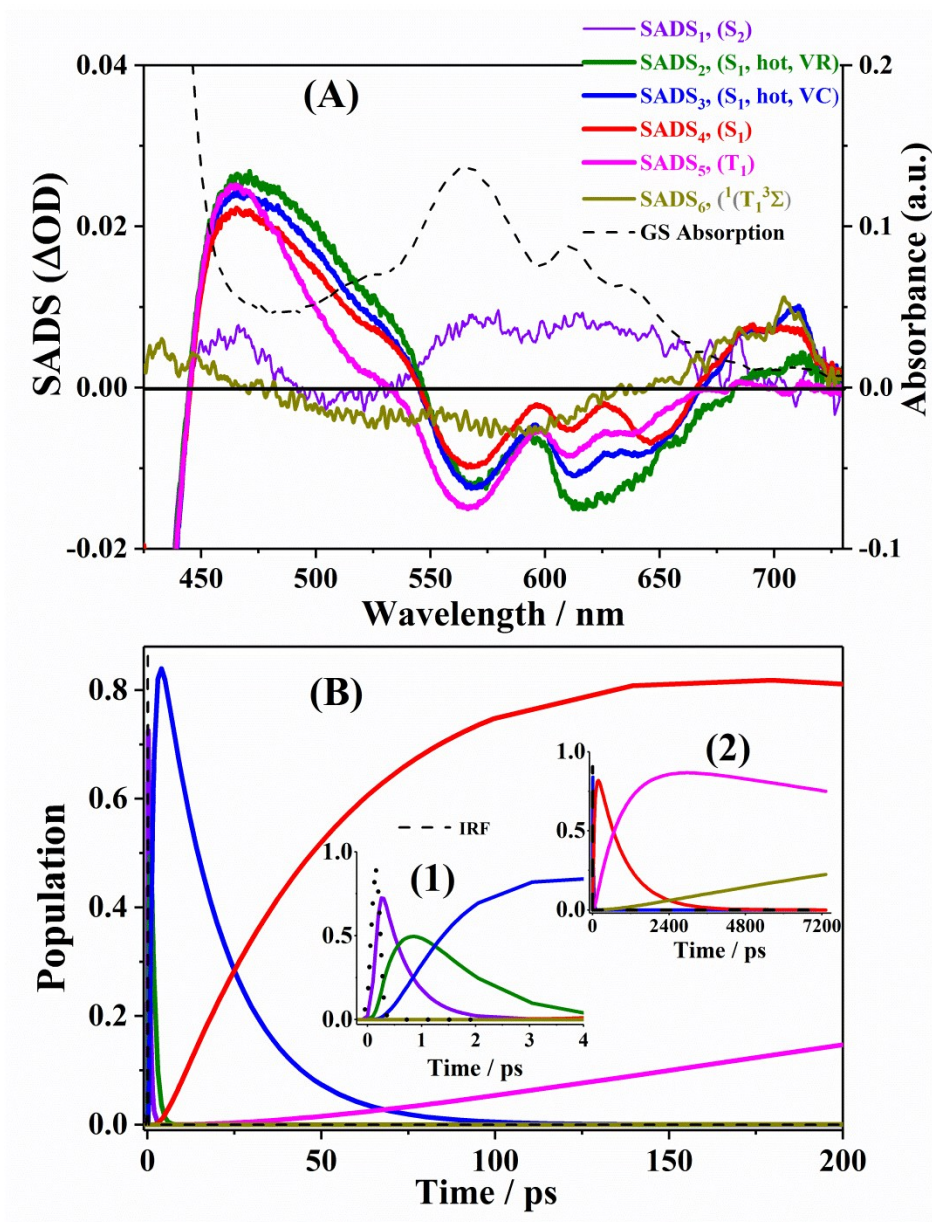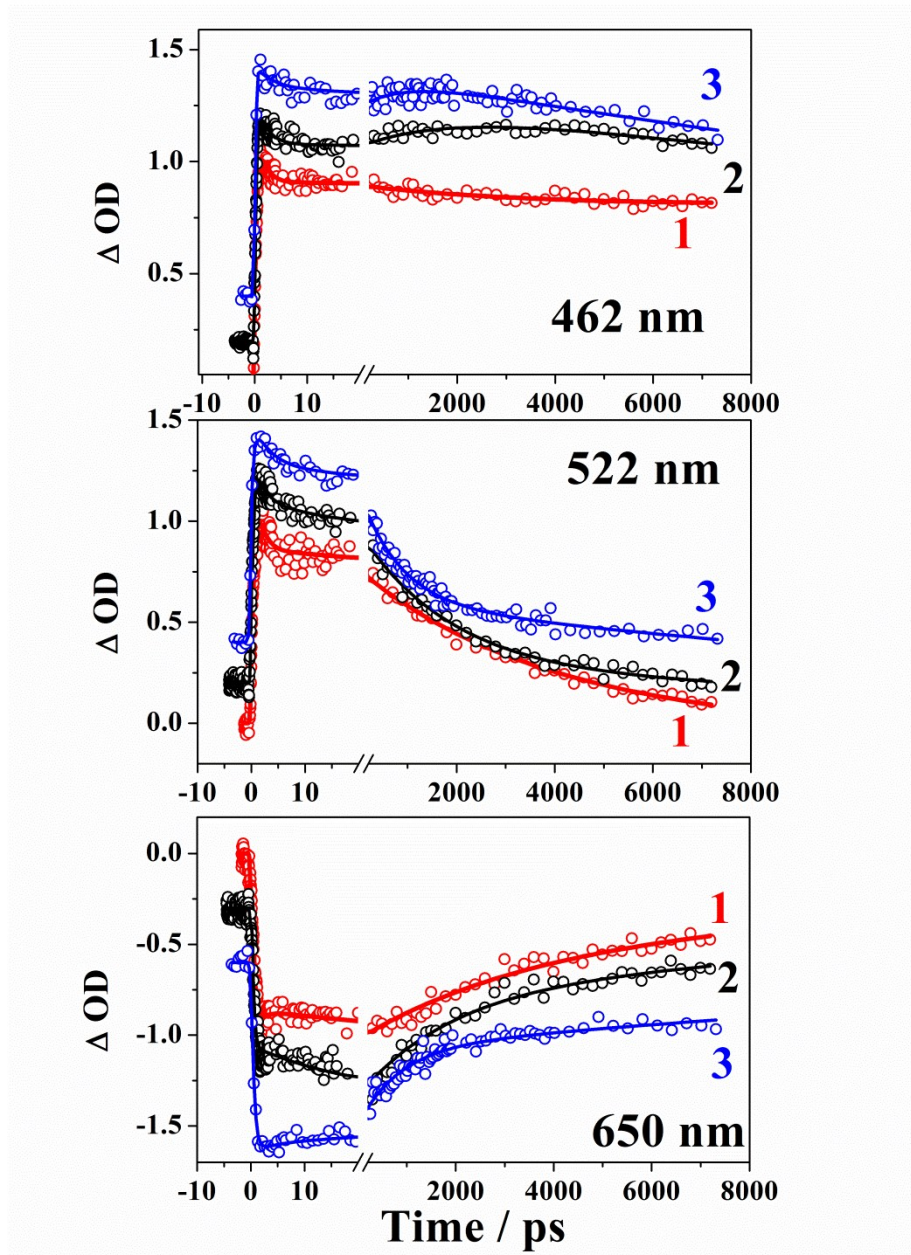
Figure S9. Normalized time profiles at several selected wavelengths of Corrole **1**-**3** in benzene after 400 nm pump.
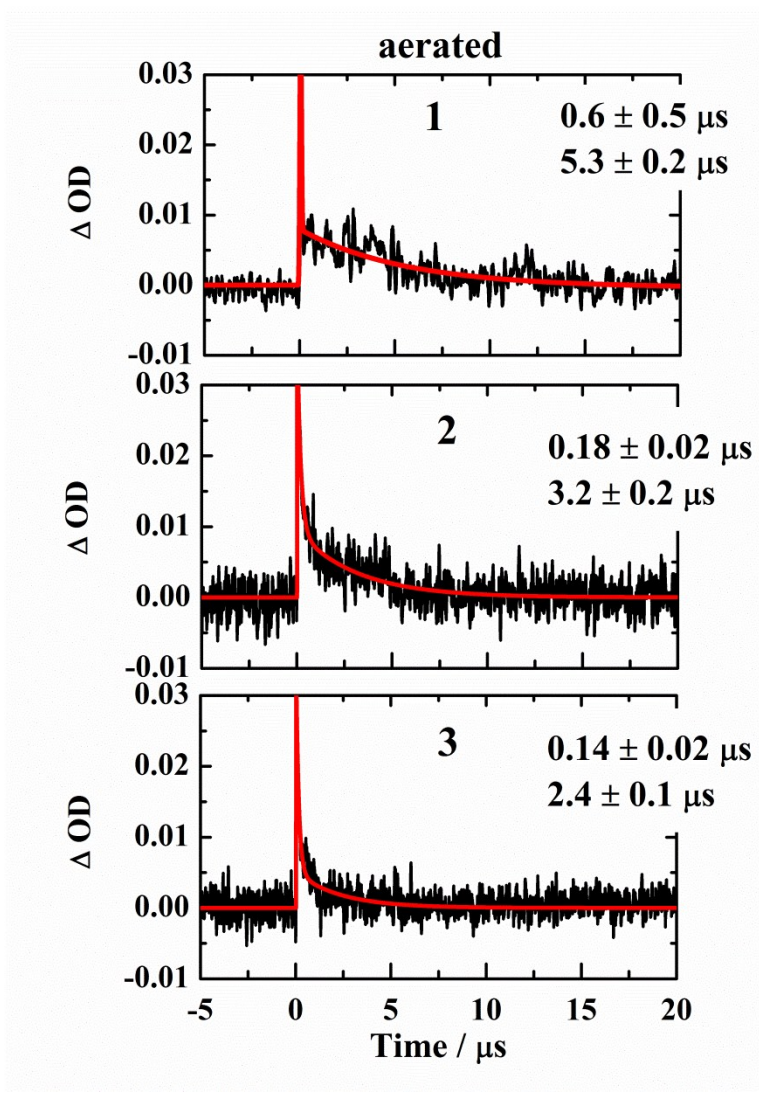
Figure S10. The microsecond time domain kinetic traces monitored at 460 nm after excitation at 532 nm for Corrole **1**-**3** in aerated benzene.

The kinetic traces were fitted by a biexponential decays. The shorter decay comes from the laser beam disturbing, and the longer one is the decay of $T_1 \rightarrow S_0$.

The comparative actinometry method to calculate the singlet oxygen quantum yields Φ$_\Delta$

From using eq 3 (comparative actinometry method), [1] the singlet oxygen quantum yields Φ$_\Delta$ can be calculated,

$$\Phi_\Delta = \Phi_\Delta^{std} \frac{I}{I_{std}} \frac{1-10^{-A^{std}}}{1-10^{-A}}$$

where Φ_Δ^{std} (0.7)[2] is the singlet oxygen quantum yield of H$_2$TPP as the standard sample in aerated toluene, I and I_{std} refer to the singlet oxygen emission intensities at the peaks for the tested sample and H$_2$TPP, respectively, and A and A^{std} stand for the ground-state absorbance of the tested sample and H$_2$TPP at the excited wavelength of 550 nm, respectively.
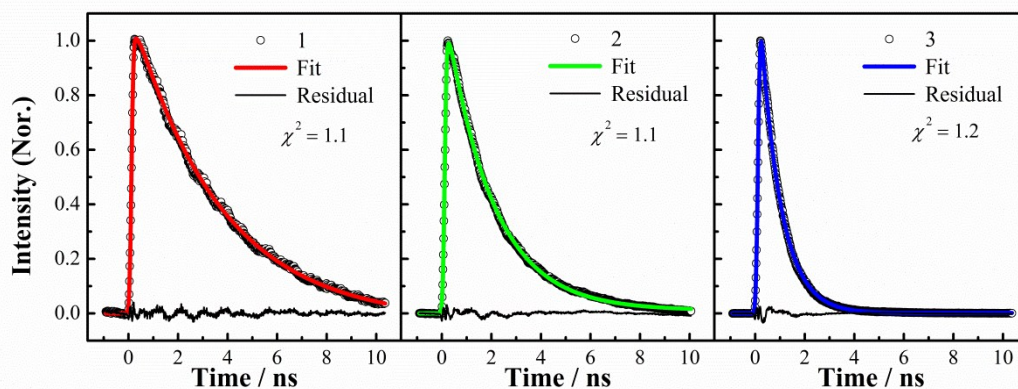
Figure S11. Fluorescence decay traces for Corroles **1**-**3** in benzene, recorded at 648 nm. The pump wavelength was 400 nm. To remove the influence of laser pulse, we fitted the curve from 0.04 ns. Open circles are observed data points; Colorful solid lines are the corresponding exponential fits. Black solid lines are residuals.

REFERENCES

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2 B. Ventura, A. Degli Esposti, B. Koszarna, D. T. Gryko and L. Flamigni, *New Journal of Chemistry*, 2005, **29**, 1559-1566.