Supplemental Information

Why does 4-biphenyl carbonyl azide have ultra-short-lived excited states? An ultrafast UV–vis spectroscopic and computational study

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1. Figure list:

Fig. S1 Transient absorption spectra of 4-BpCON$_3$ in cyclohexene after 308 nm excitation (a) and time course at 465 nm for transient absorption (TA) (b) respectively.

Fig. S2 2-D transient absorption spectra of 4-biphenyl oxadiazole in acetonitrile. The pump wavelength is 282 nm.

Fig. S3 2-D transient absorption spectra of 4-biphenyl isocyanate in acetonitrile. The pump wavelength is 308 nm.

Fig. S4 2-D transient absorption spectra of 4-biphenyl carboxamide in acetonitrile. The pump wavelength is 270 nm.

Fig. S5 Comparison of UV-vis absorption of 4-biphenyl carbonyl azide (4-BpCON$_3$) and its photolysis products: 4-biphenyl oxadiazole (BpOx), 4-biphenyl isocyanate (BpNCO), and 4-biphenyl carboxamide (BpCONH$_2$) in acetonitrile.

Fig. S6 Transient absorption spectra of 4-BpCON$_3$ in CHCl$_3$ after 308 nm excitation. (1.a) and (1.b) are TA and time course at 465 nm in CHCl$_3$ (Amylene as stabilizer). (2.a) and (2.b) are TA and time course at 460 nm in CHCl$_3$ (EtOH as stabilizer).

Fig. S7 UV-vis absorption spectra of 4-biphenyl carbonyl azide (4-$BpCON_3$) in different solvents: CHCl3, MeOH, acetonitrile (ACN), and cyclohexane (cHexane). The wavelength of maximum absorption is shown in parenthesizes.

Fig. S8 2-D transient absorption spectra of 4-$BpCON_3$ in MeOH. The pump wavelength is 308 nm (a) and 270 nm (b). A slow decay component is seen upon 270 nm excitation.

Fig. S9 2-D transient absorption spectra of 4-$BpCON_3$ in acetonitrile. The pump wavelength is 308 nm in (a) and 270 nm in (b) respectively. The transient absorption of 4-biphenyl oxadiazole (BpOx) appears in both cases.

Fig. S10 Transient absorption spectra of fluorene-2-carbonyl azide ($F2CON_3$) in acetonitrile after 308 nm excitation (a), time course at 435 nm for transient absorption (TA) (b), and time course for the stimulated emission (SE) at 370 nm (c) respectively.

Fig. S11 UV-vis absorption spectra of 4-biphenyl carbonyl azide (4-$BpCON_3$), fluorene-2-carbonyl azide ($F2CON_3$), 2-naphthalene sulfonyl azide (2-$NpSO_2N_3$), and 2-naphthalene carbonyl azide (2-$NpCON_3$) in acetonitrile.

Fig. S12 Structural information of $MeCON_3$, $PhCON_3$, 4-$BpCON_3$, and 2-$NpCON_3$ at their ground stats (S_0 structure at PBE0/ def2-TZVP level) and relaxed excited states (S_1) at cam-B3LYP/ def2-TZVP level. Units: bond length, Å ; NNN angle, degrees(°). The dipole moment (μ) in Debye and ΔE, the relative energy against the ground state (S_0) in Kcal/mol were calculate at CAM-B3LYP/ def2-TZVP level and are also given.

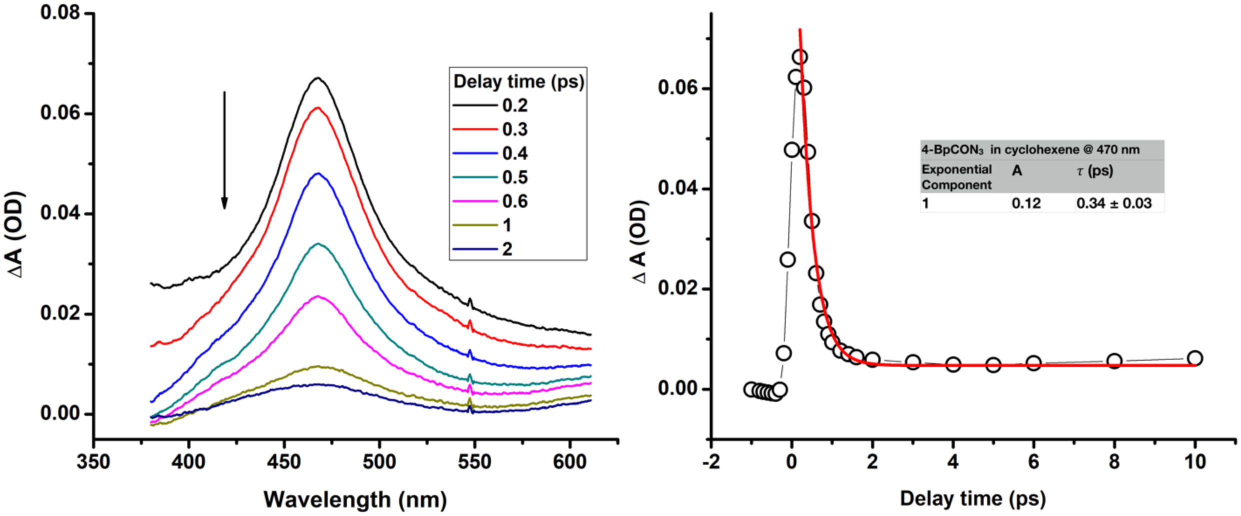
Fig. S13 Comparison of potential energy surfaces of π(**Ar**)π* and n(**CO**)π* S_1 states of $F2CON_3$ and 2-$NpCON_3$.

2. **Table S1.** TDDFT results of lowest electronic transitions of selected molecules.

3. Synthesis of 2-biphenyl-5-methyl-1,3,4-oxadiazole (BpOx)

   Scheme S1. Synthesis of 2-biphenyl-5-methyl-1,3,4-oxadiazole (BpOx)

   Scheme S2. Photolysis of carbonyl azides produces BpOx in acetonitrile (ACN).



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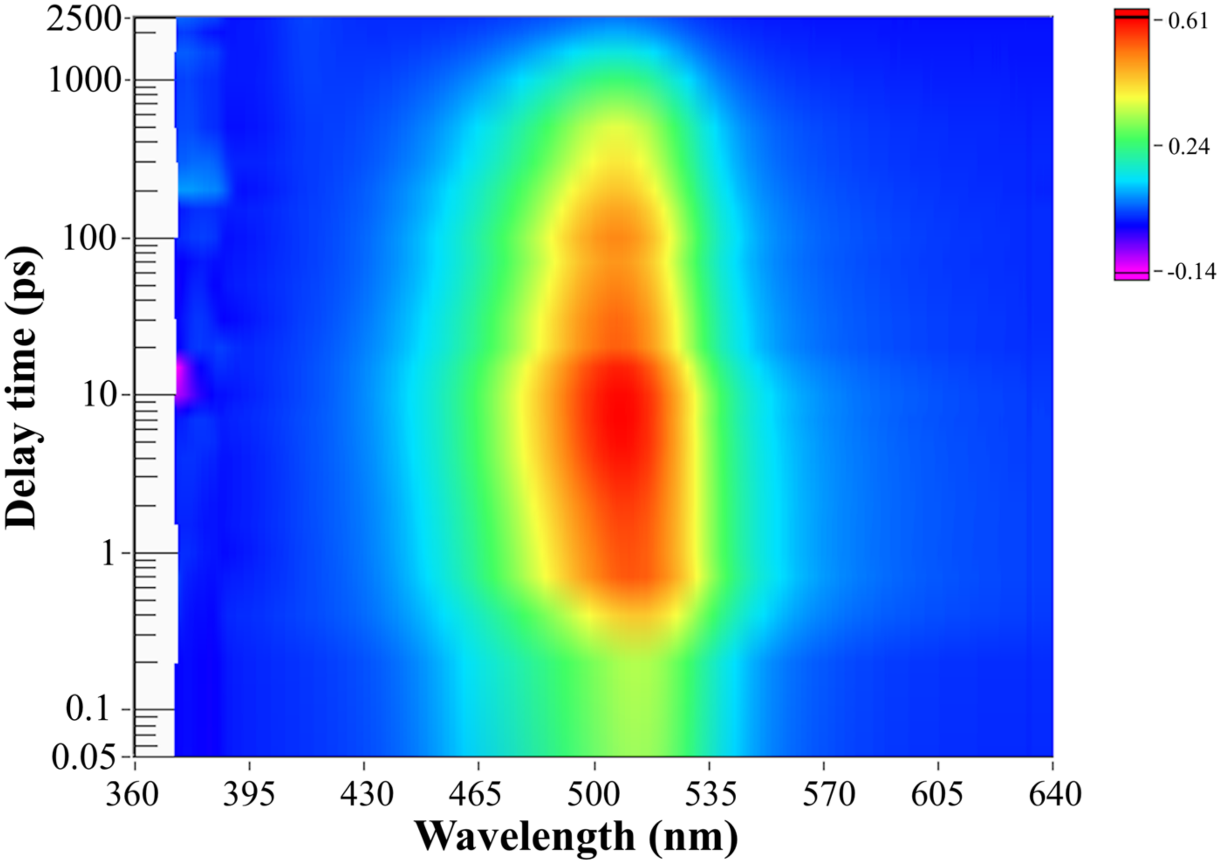


Fig. S2 2-D transient absorption spectra of 4-biphenyl oxadiazole in acetonitrile. The pump wavelength is 282 nm.

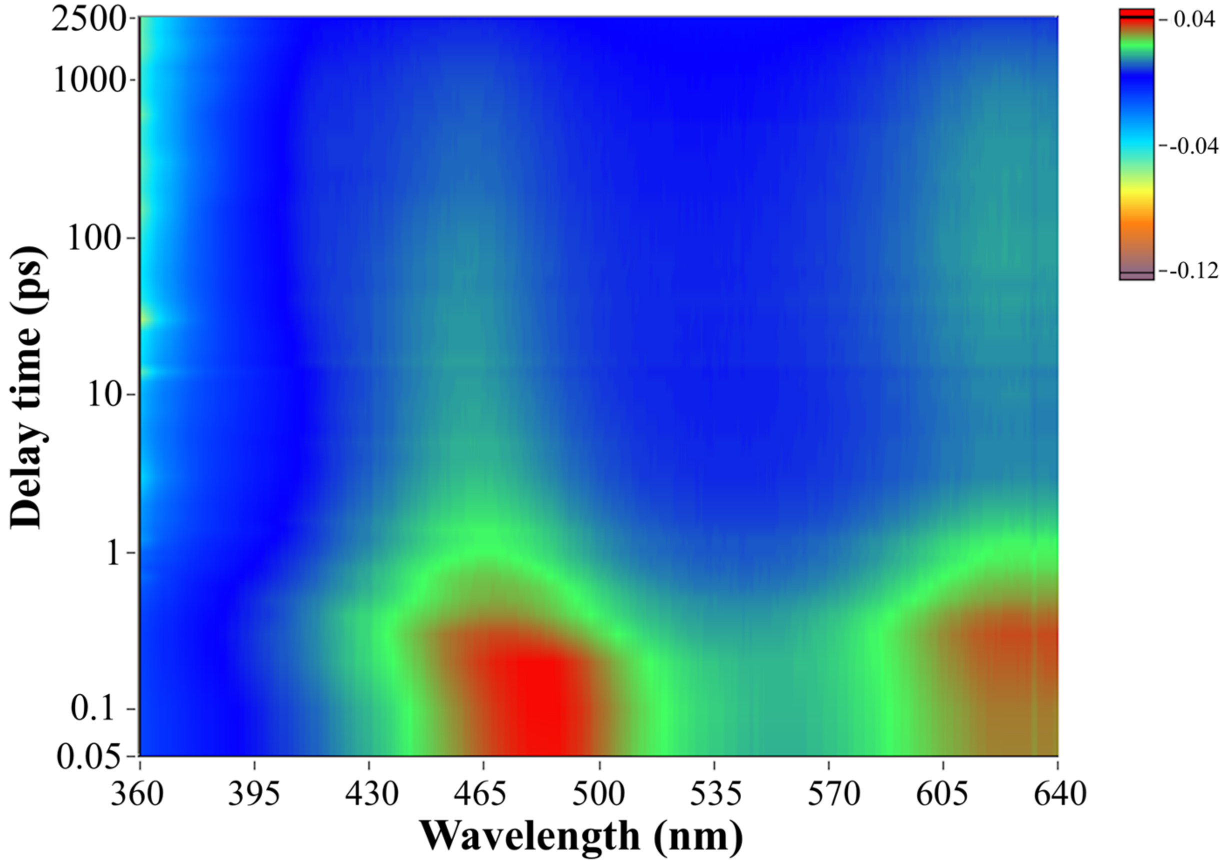


Fig. S3 2-D transient absorption spectra of 4-biphenyl isocyanate in acetonitrile. The pump wavelength is 308 nm.

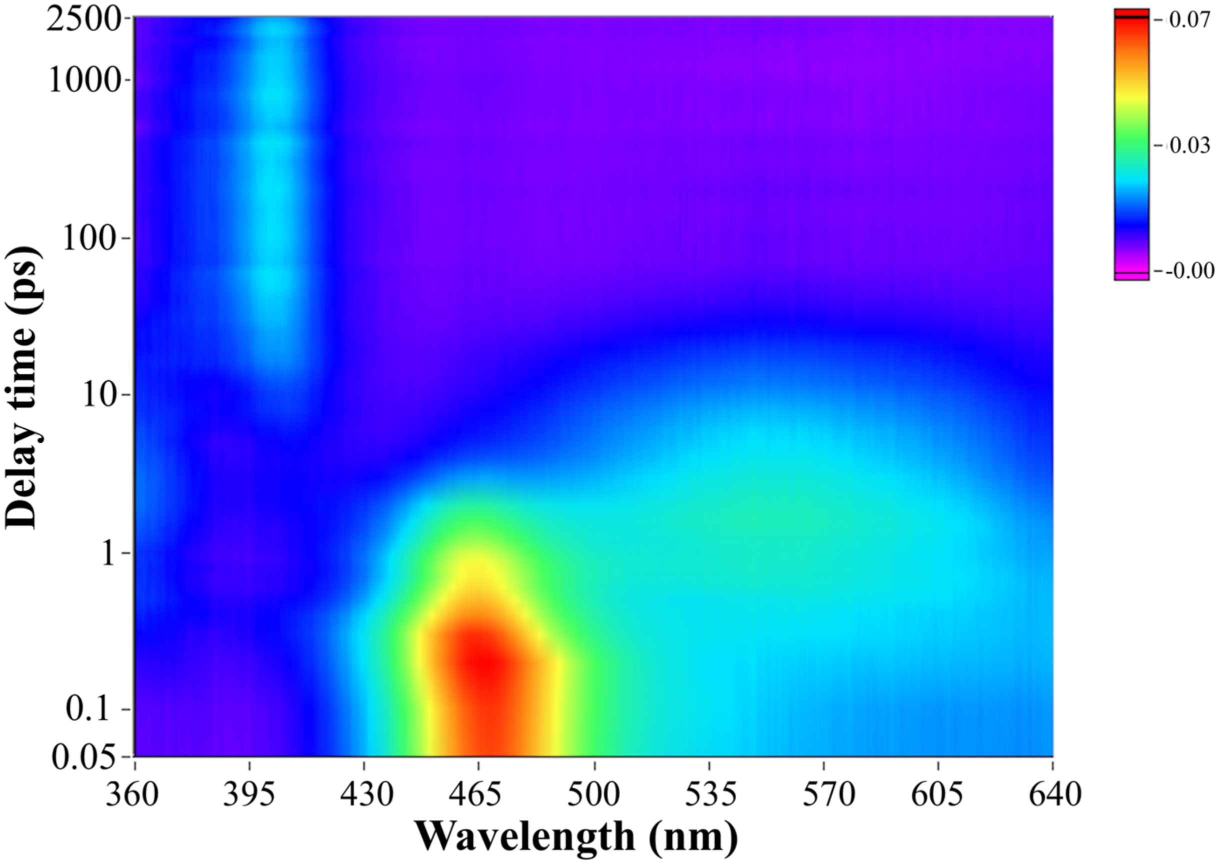
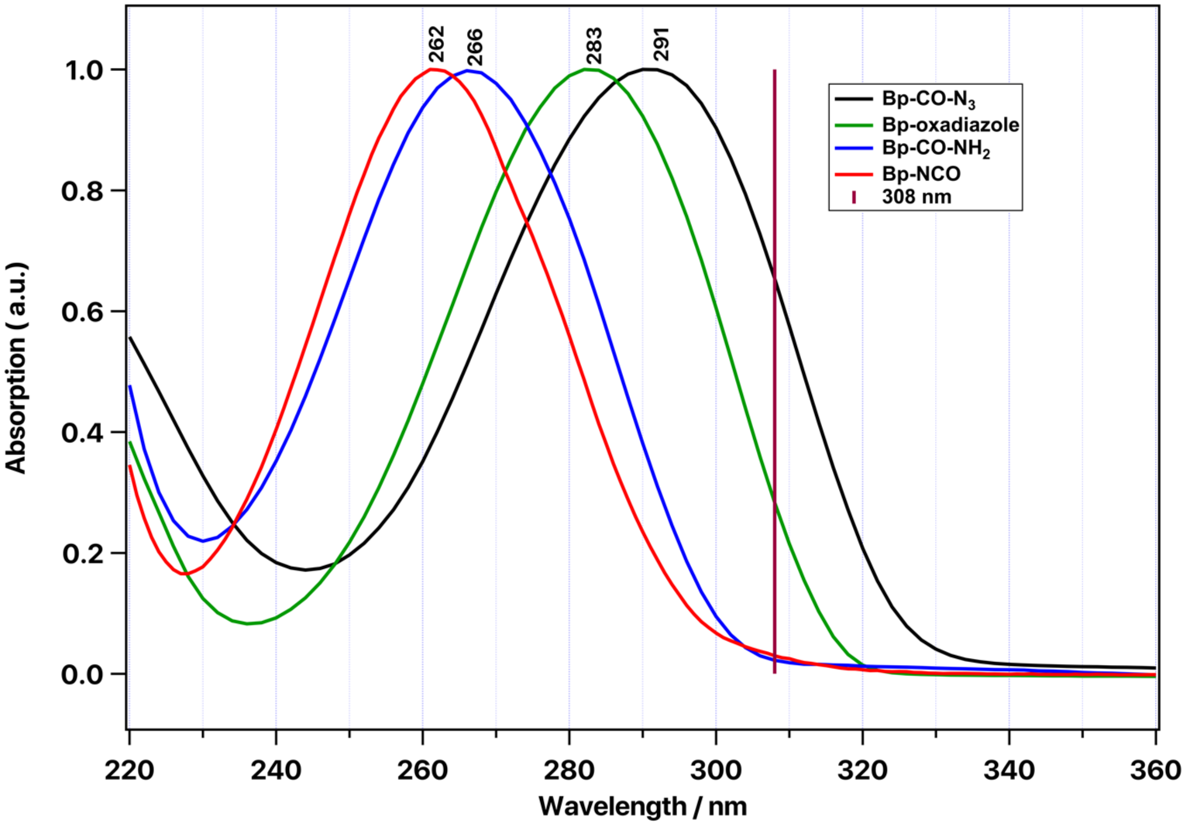


Fig. S4 2-D transient absorption spectra of 4-biphenyl carboxamide in acetonitrile. The pump wavelength is 270 nm.



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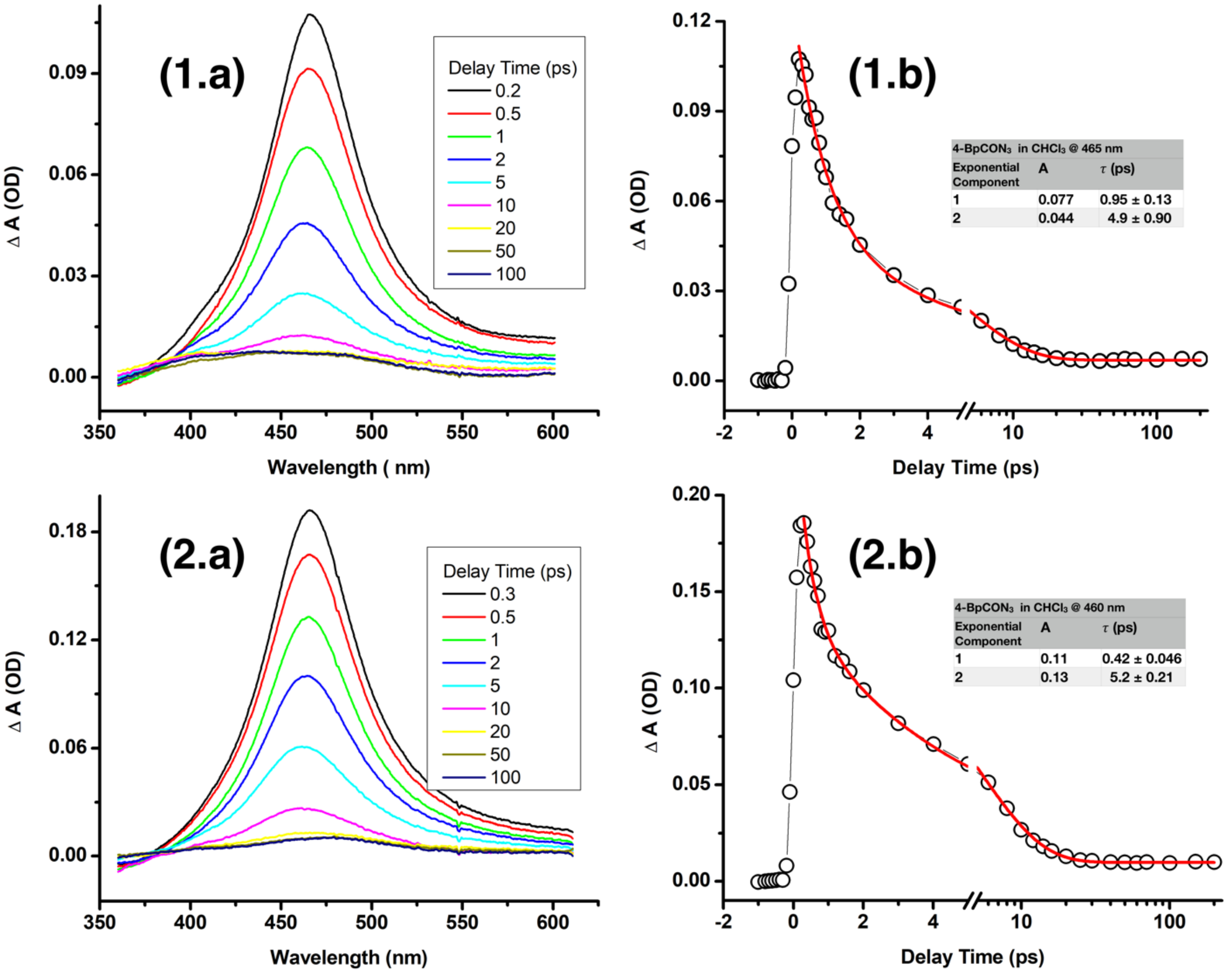


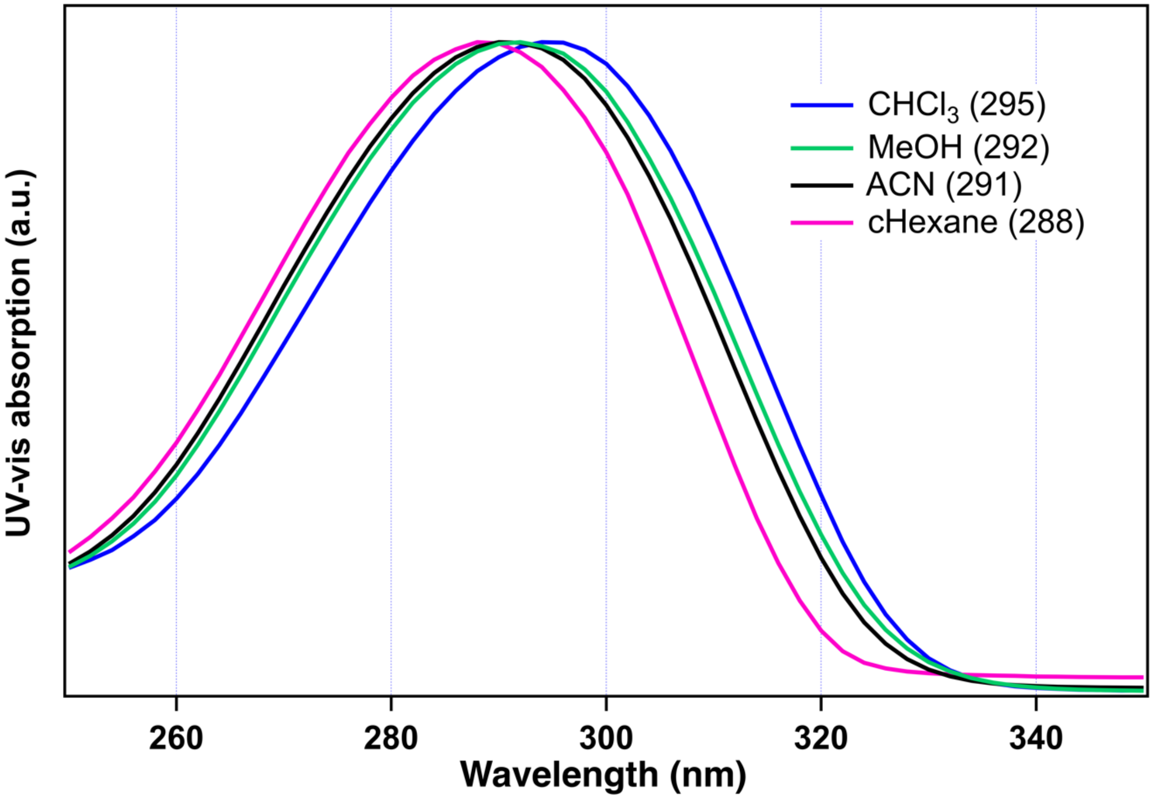
4-BpCON$_3$ in CHCl$_3$ @ 465 nm

Exponential Component	A	τ (ps)
1	0.077	0.95 ± 0.13
2	0.044	4.9 ± 0.90

4-BpCON$_3$ in CHCl$_3$ @ 460 nm

Exponential Component	A	τ (ps)
1	0.11	0.42 ± 0.046
2	0.13	5.2 ± 0.21

Fig. S6 Transient absorption spectra of 4-BpCON$_3$ in CHCl$_3$ after 308 nm excitation. (1.a) and (1.b) are TA and time course at 465 nm in CHCl$_3$ (Amylene as stabilizer). (2.a) and (2.b) are TA and time course at 460 nm in CHCl$_3$ (EtOH as stabilizer).



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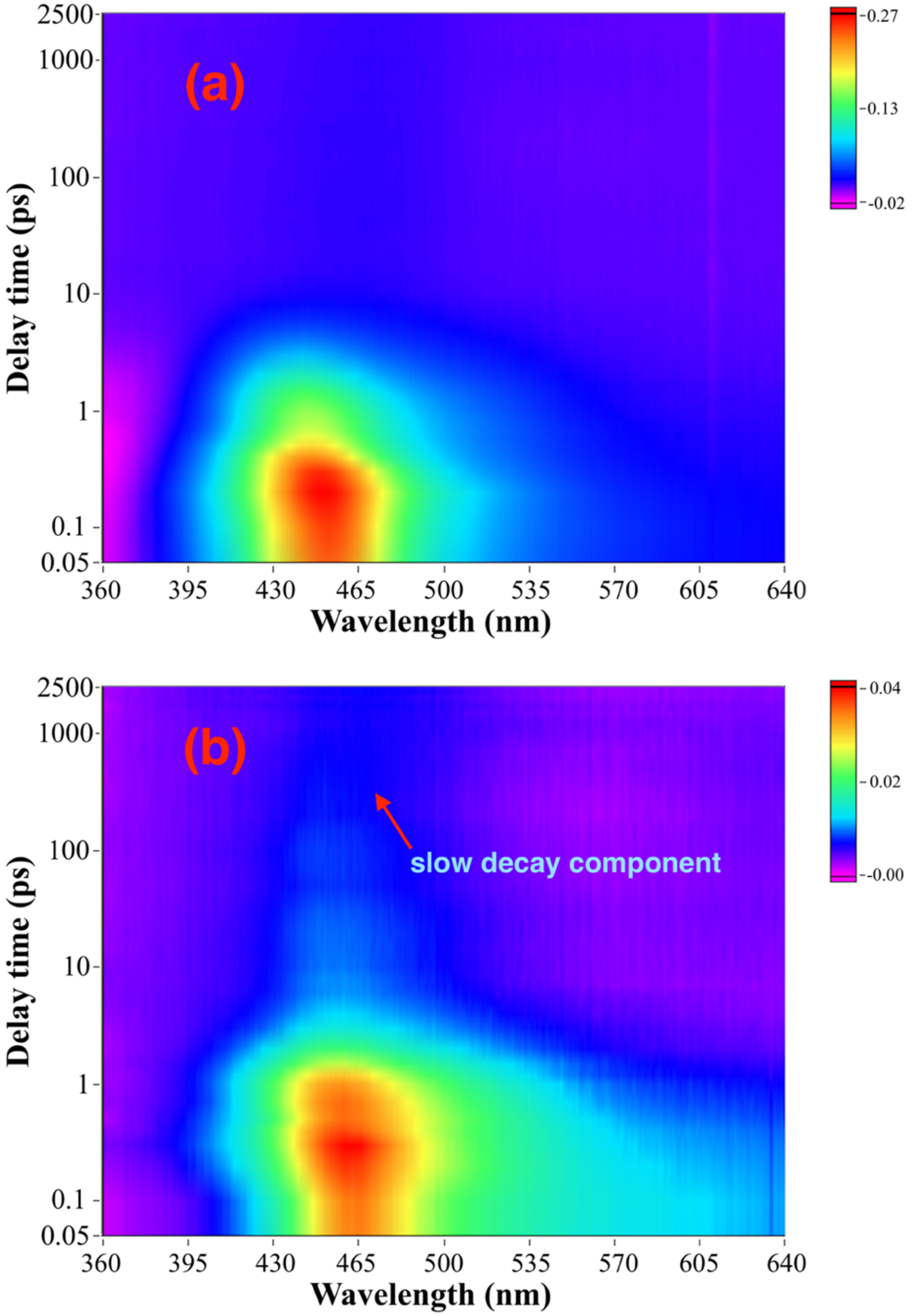


Fig. S8 2-D transient absorption spectra of 4-BpCON$_3$ in MeOH. The pump wavelength is 308 nm (a) and 270 nm (b). Red-shifted TA and a slow decaying component can be seen upon 270 nm excitation. Selected lifetimes upon 270 nm excitation: τ (600 nm, decay) =1.2 ± 0.05 ps; τ (450 nm, decay) = 1.5 ± 0.1 ps. Maximum absorption is reached at 0.2 and 0.3 ps with 308 nm excitation and 270 nm excitation respectively.

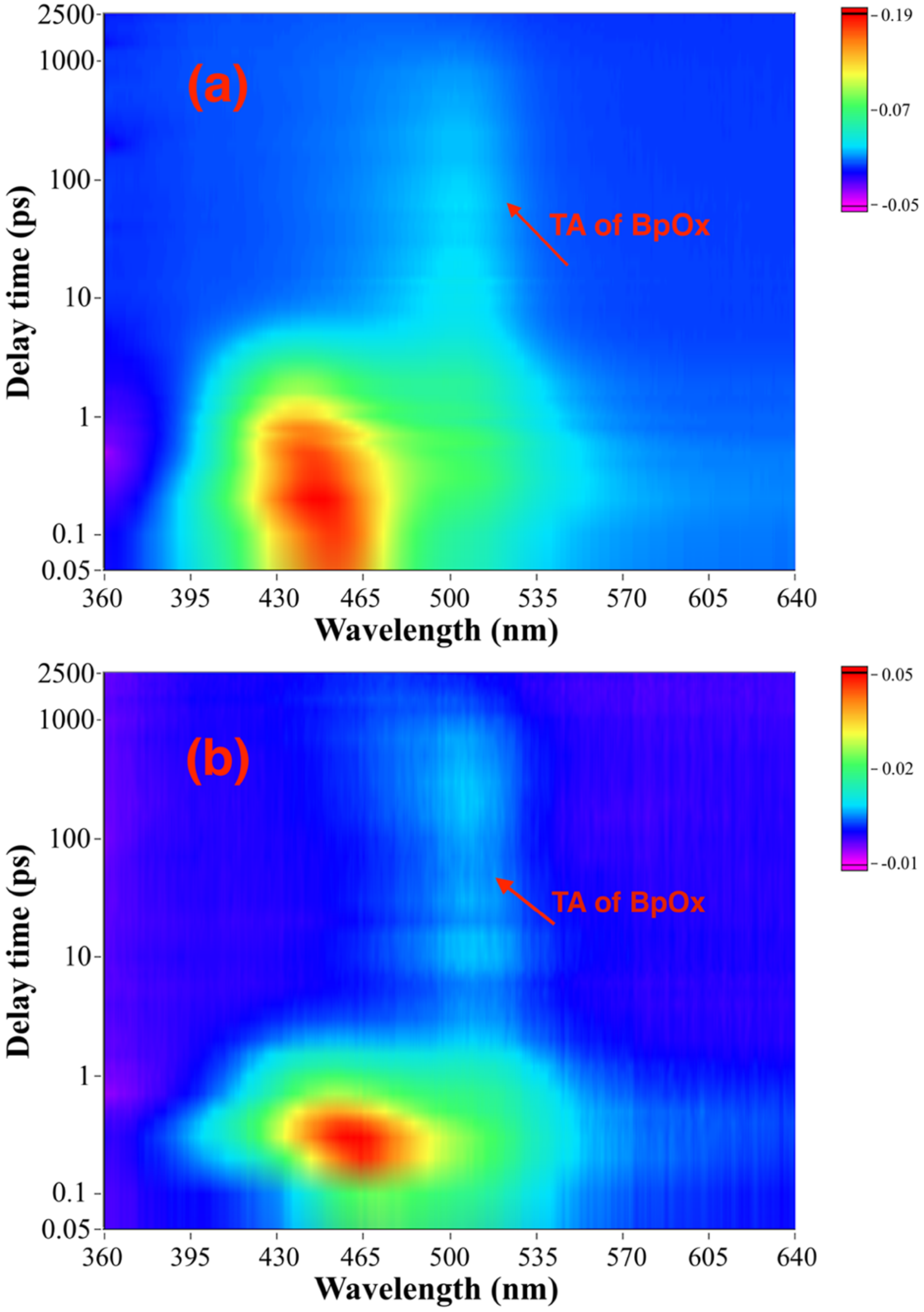
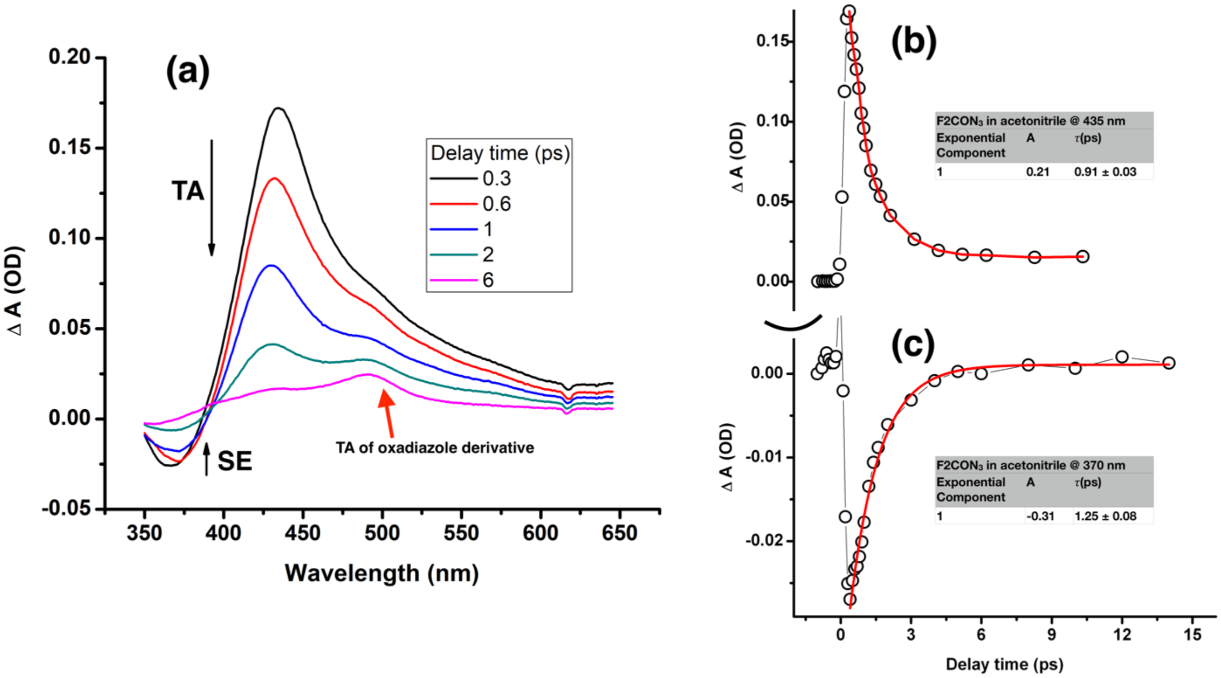


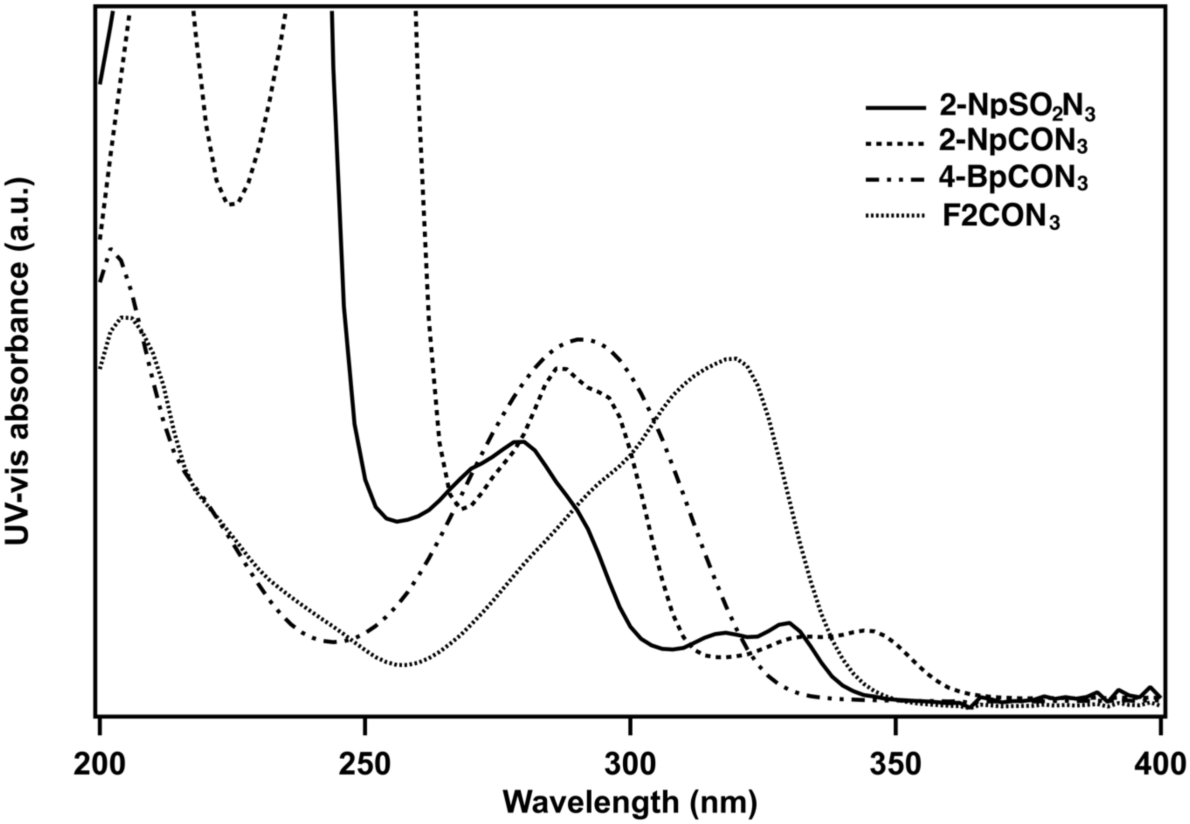
Fig. S9 2-D transient absorption spectra of 4-BpCON$_3$ in acetonitrile. The pump wavelength is 308 nm in (a) and 270 nm in (b) respectively. The transient absorption of 4-biphenyl oxadiazole (BpOx) appears in both cases. Red-shifted TA can be seen upon 270 nm excitation. Selected lifetimes upon 270 nm excitation: τ (450 nm, decay) = 0.83 ± 0.03 ps. Maximum absorption is reached at 0.3 and 0.5 ps with 308 nm excitation and 270 nm excitation respectively.



F2CON$_3$ in acetonitrile @ 435 nm		
Exponential Component	A	τ(ps)
1	0.21	0.91 ± 0.03

F2CON$_3$ in acetonitrile @ 370 nm		
Exponential Component	A	τ(ps)
1	-0.31	1.25 ± 0.08

Fig. S10 Transient absorption spectra of fluorene-2-carbonyl azide (F2CON$_3$) in acetonitrile after 308 nm excitation (a), time course at 435 nm for transient absorption (TA) (b), and time course for the stimulated emission (SE) at 370 nm (c) respectively.



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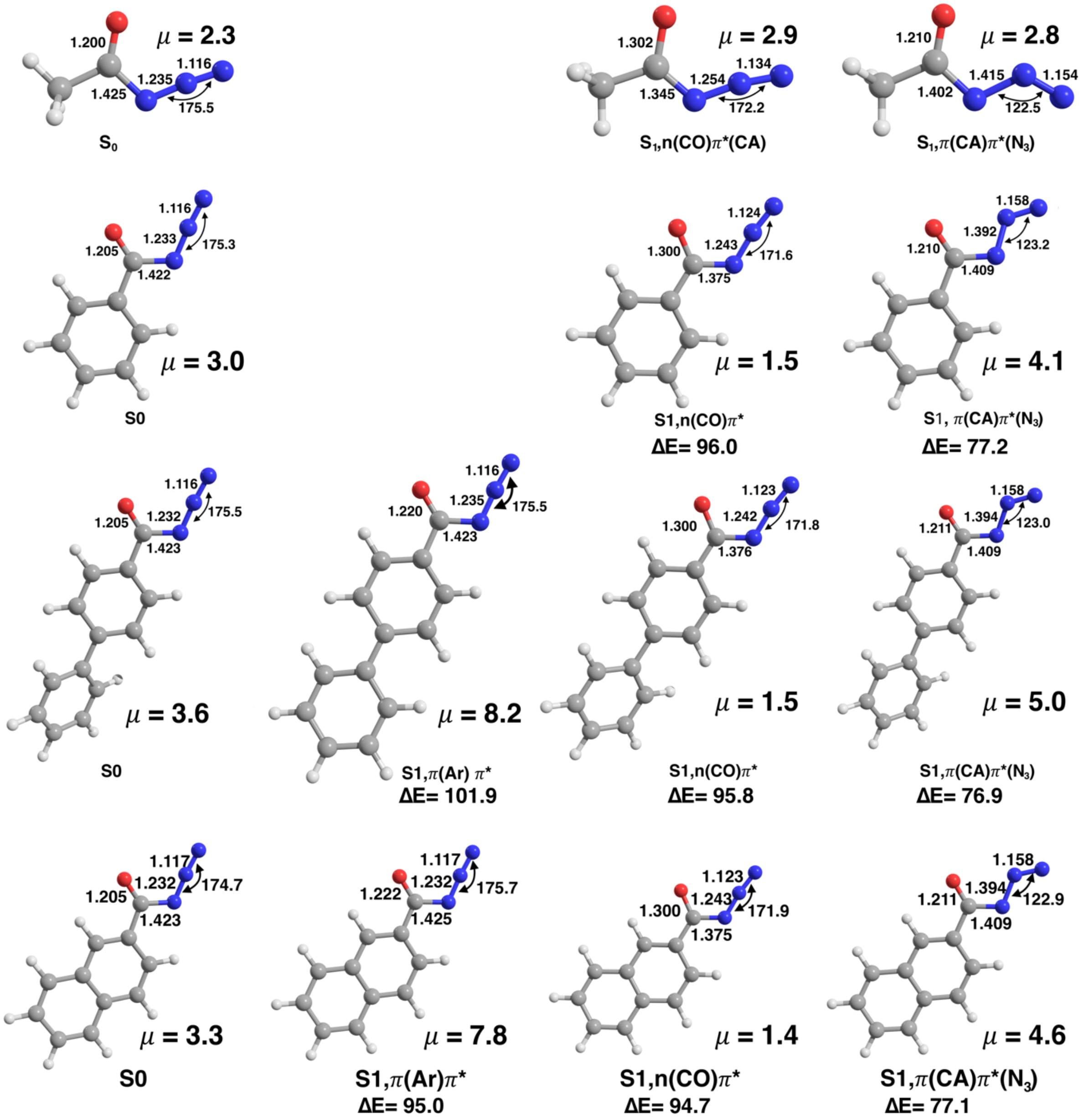


Fig. S12 Structural information of $MeCON_3$, $PhCON_3$, 4-$BpCON_3$, and 2-$NpCON_3$ at their ground stats (S_0 structure at PBE0/ def2-TZVP level) and relaxed excited states (S_1) at cam-B3LYP/ def2-TZVP level. Units: bond length, Å ; NNN angle, degrees(°). The dipole moment (μ) in Debye and ΔE, the relative energy against the ground state (S_0) in Kcal/mol were calculate at CAM-B3LYP/ def2-TZVP level and are also given.

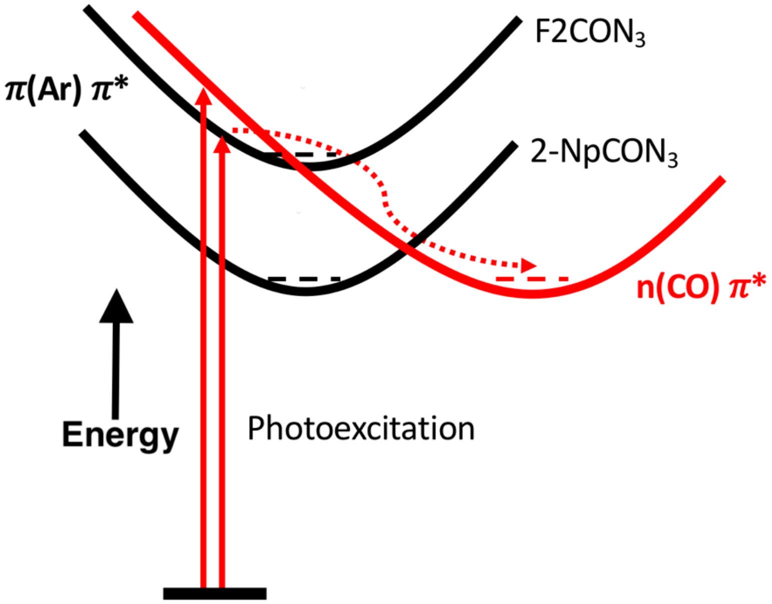


Fig. S13 Comparison of potential energy surfaces of π(**Ar**)π* and n(**CO**)π* S_1 states of $F2CON_3$ and $2\text{-}NpCON_3$.

Table S1 TDDFT results of lowest electronic transitions of selected molecules.

1. **Biphenyl**

Theory	S1		S2		S3	
	Energy (nm)	f	Energy (nm)	f	Energy (nm)	f
Experimental UV-vis peaks	247.5[a]					
B3LYP	**251**	**0**	**247**	**0**	244	0.55
BLYP	**273**	**0**	**269**	**0**	**261**	**0.51**
BP86	**271**	**0**	**267**	**0**	**259**	**0.52**
[a] J.M. Dixon, M. Taniguchi and J. S. Lindsey, *Photochem. Photobiol.*, 2005, **81**, 212-213.						

2. **Fluorene**

Theory	S1		S2		S3	
	Energy (nm)	f	Energy (nm)	f	Energy (nm)	f
Experimental observation	**296**[b]					
B3LYP	**271**	**0.088**	**254**	**0.47**		
PBE0	264	0.11	249	0.46		
ωB97x	246	0.21	233	0.31		
LC-BLYP	249	0.17	237	0.0040		
TPSS	285	0.043	268	0.0085	262	0.50
BLYP	**294**	**0.039**	**276**	**0.0079**	**268**	**0.49**
BP86	**291**	**0.042**	**274**	**0.0085**	**266**	**0.50**
PBE	**291**	**0.042**	**274**	**0.0085**	**265**	**0.50**
[b] C. A. Pinkham and S. C. Wait Jr, *J. Mol. Spectrosc.*, 1968, **27**, 326–342.						

	S1		S2		S3	
Molecule / Theory	Energy (nm)	f	Energy (nm)	f	Energy (nm)	f
3. MeCON$_3$ **/ PBE0**	**258**[c]	**0**	**237**	**0**		
4. PhCON$_3$ /PBE0	285[c]	0	256	0.019		
5. 2-NpCON$_3$ **/ B3LYP**	**322**[d]	**0.062**	**299**[a]	**0**	288	0.15
6. 2-NpCON$_3$ / PBE0	320[d]	0.066	293[a]	0	281	0.14
7. 4- BpNH$_2$ /PBE0	271[e]	0.062	256	0.69		
8. 4- BpNCO /PBE0	257	0.44	254	0.49		

MeCON$_3$ = methyl carbonyl azide; PhCON$_3$ = benzoyl azide; 2-NpCON$_3$ = 2-naphthoyl azide; 4-BpNH$_2$ = 4-biphenyl amide; 4-BpNCO = 4-biphenyl isocyanate.

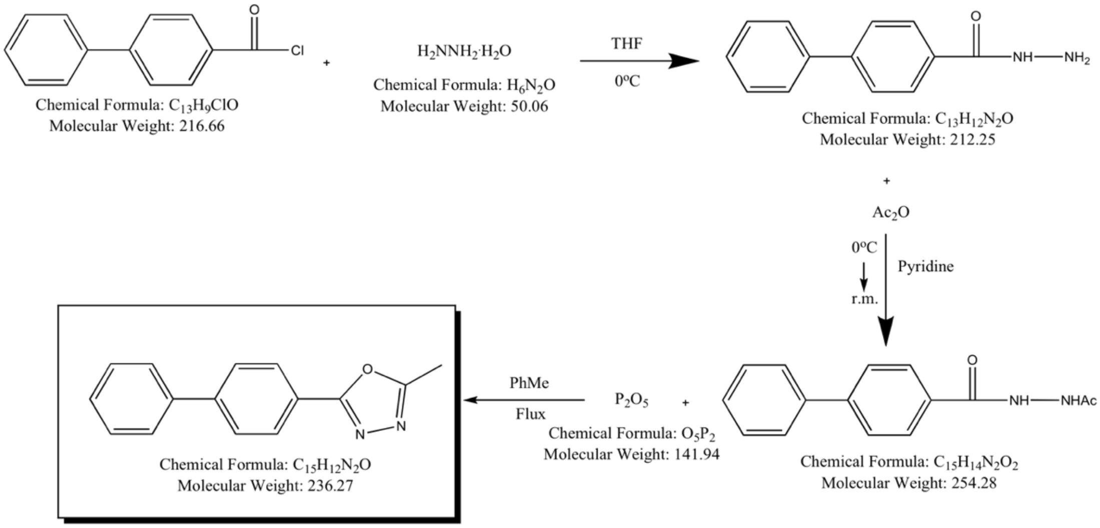
[c] n(**CON$_3$**)- π* transition;

[d] π(**naphthalene**)-π* transition;

[e] n(**amide**)- π* transition.

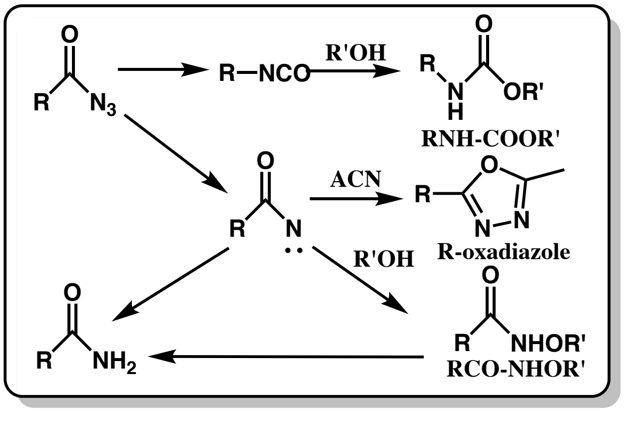
Synthesis of 2-biphenyl-5-methyl-1,3,4-oxadiazole (BpOx)

The synthesis basically followed the processes (Scheme 1) described in two papers.[1, 2]



Scheme S1. Synthesis of 2-biphenyl-5-methyl-1,3,4-oxadiazole (BpOx)

The final product was purified by column chromatography on silica gel (eluent: hexanes:AcOEt=1:3 (v:v)). ^{1}H-NMR (250MHz, $CDCl_3$): δ 2.62 (3H, s), 7.34-7.50 (3H, m), 7.59-7.65 (2H, m), 7.68-7.74 (2H, m), 8.05-8.11 (2H, m). IR (thin film): 1614, 1589, 1580*, 1570, 1485*, 1450, 1412, 1250, 1091, 958, 846, 773, 734 cm^{-1}.



Scheme S2. Photolysis of carbonyl azides produces BpOx in acetonitrile (ACN).

Reference:

1 D. H. Christensen, J. T. Nielsen and O. F. Nielsen, *J. Mol. Spectrosc.*, 1967, **24**, 225-234.

2 A. Kakefuda, *Biorg. Med. Chem.*, 2002, **10**, 1905-1912.