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

Supporting Information

Substituent Control of ultrafast twisted intramolecular charge transfer rates in dimethylaminochalcone derivatives

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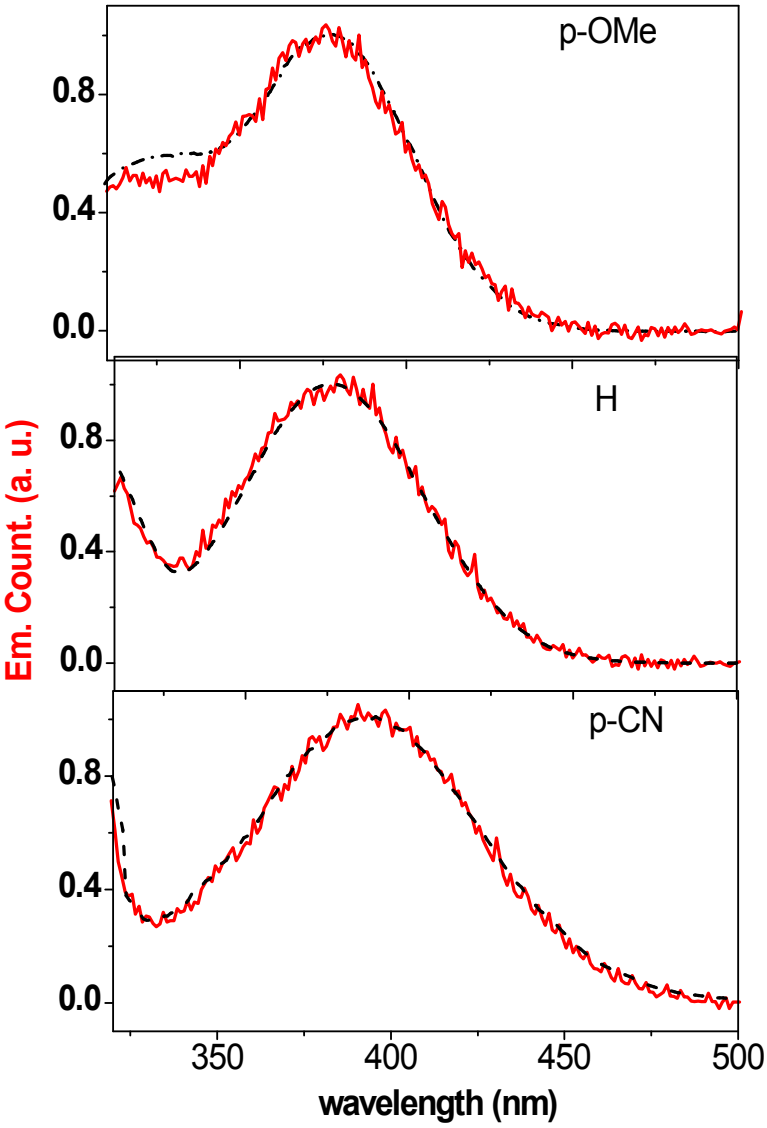


Figure S1: Excitation spectra (red lines) of three DMAC derivatives in acetonitrile. Absorption spectra (black dashed line) were also shown for comparison.

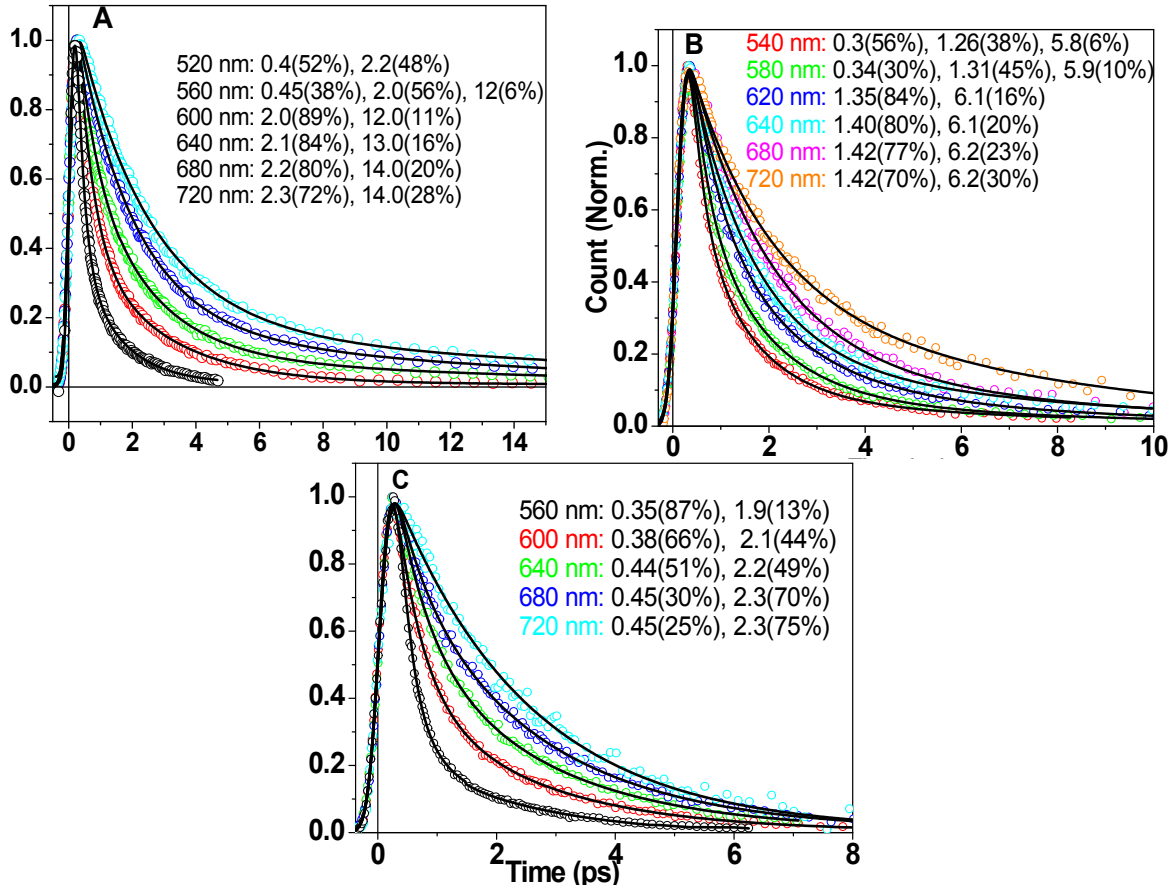
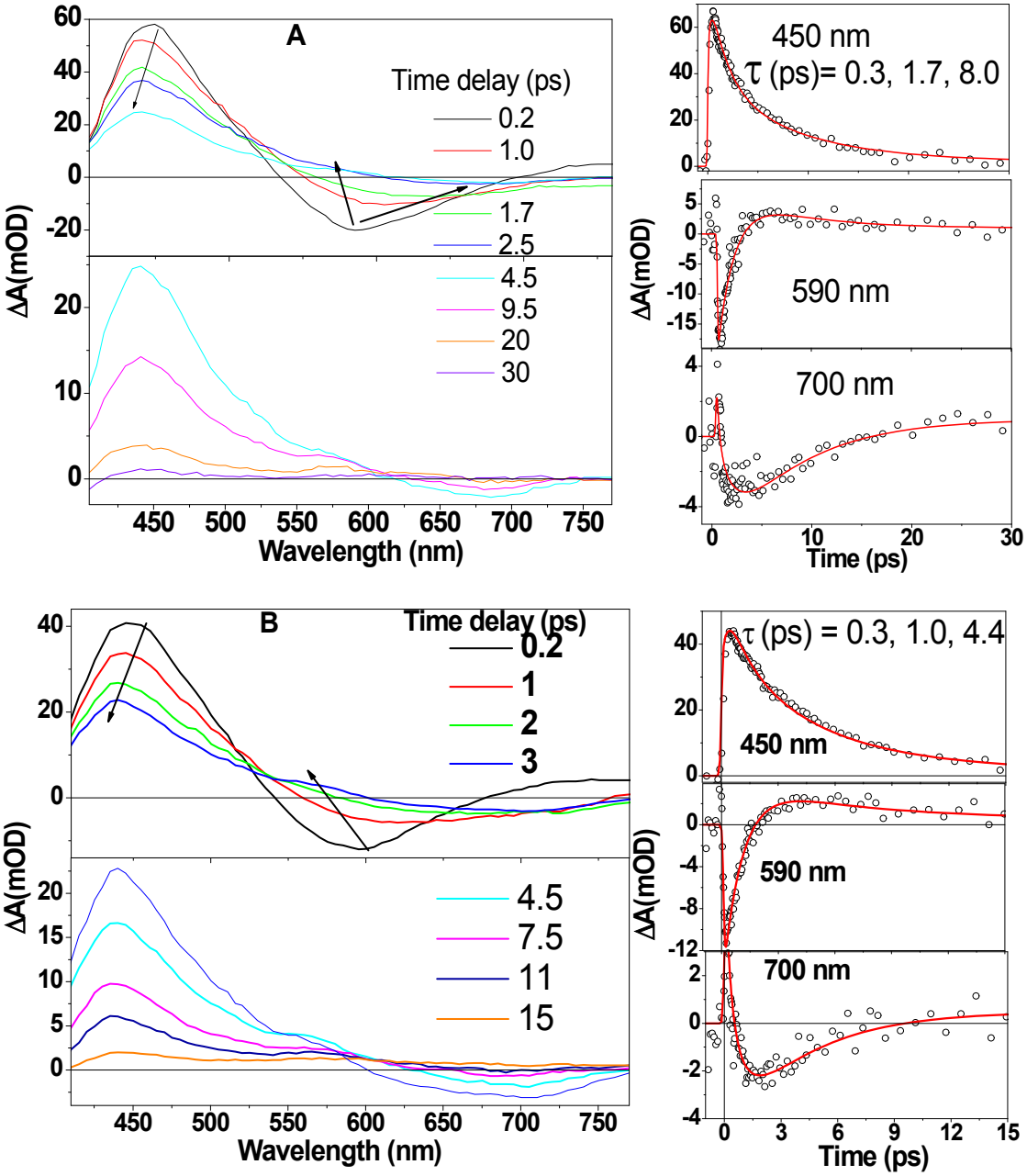


Figure S2: Wavelength dependent transient emission kinetics of (A) ***p*-OMe**, (B) **H** and (C) ***p*-CN** recorded by fluorescence upconversion technique. λ_{ex} = 390 nm. Lifetime (in ps) and amplitudes at different wavelengths obtained from multiexponential fitting


A
Time delay (ps)
0.2
1.0
1.7
2.5
4.5
9.5
20
30
ΔA(mOD)
Wavelength (nm)
450 nm
τ (ps)= 0.3, 1.7, 8.0
590 nm
700 nm
Time (ps)
B
Time delay (ps)
0.2
1
2
3
4.5
7.5
11
15
ΔA(mOD)
Wavelength (nm)
τ (ps) = 0.3, 1.0, 4.4
450 nm
590 nm
700 nm
Time (ps)

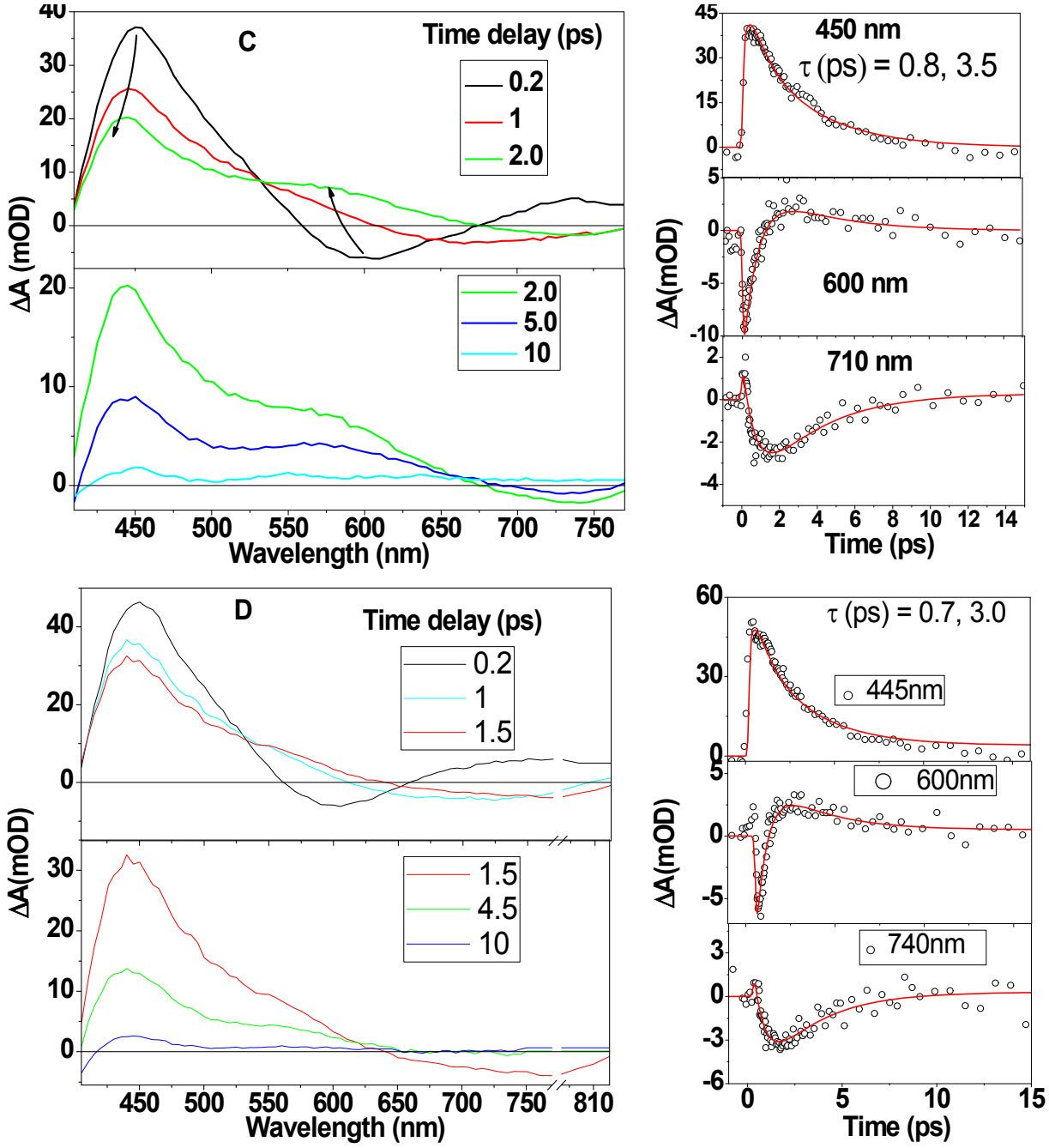


Figure S3: Transient absorption spectra (left) and kinetics (right) of four DMAC derivatives. (A) ***p*-Et**, (B) ***m*-OMe**, (C) ***m*-Cl** (D) ***m*-CN**. λ_{ex} = 390 nm.

Table S1: Comparison of Stokes shiftof three of the DMAC derivatives in nonpolar toluene and polar acetonitrile

Compound	Toluene			Acetonitrile		
	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})
p-OMe	360	420	3968	376	533	7834
H	362	426	4150	378	544	8072
p-CN	386	454	3880	393	604	8889

Table S2. Summary of the time constants obtained from ultrafast transient absorption experiments of DMAC derivatives in acetonitrile.

Compound	τ_1 (ps)[a]	τ_2 (ps)[b]	τ_3 (ps)
p-OMe	0.35 ± 0.05	2.0 ± 0.1	14 ± 1
p-Et	0.32 ± 0.05	1.7 ± 0.1	8.0 ± 1
H	0.33 ± 0.05	1.3 ± 0.05	6.0 ± 0.5
p-F	0.32 ± 0.05	1.25 ± 0.05	5.8 ± 0.3
m-OMe	0.30 ± 0.05	1.0 ± 0.05	4.4 ± 0.3
m-Cl	-----	0.8 ± 0.03	3.5± 0.2
m-CN	-----	0.7 ± 0.03	3.0 ± 0.1
p-CN	----	0.42 ± 0.02	2.35 ± 0.2
[a] τ_1 corresponds to solvation time. In m-Cl, m_CN and p-CN, solvation component could not be resolved well due to occurrence of fast TICT relaxation. [b] τ_2 corresponds to ICT to TICT relaxation time, [c] τ_3 corresponds to decay of the TICT state to ground electronic state.			

Table S3: Twisting time of DMAC derivatives in polar solvents with different viscosity.

Solvent	Twisting time (ps)				
	ε,	η	*p*-OMe	H	*p*-CN
Acetonitrile	37.5	0.4	2.2	1.35	0.45
Dimethyl formamide	38	0.8	4.8	3.1	1.1
Dimethylsulphoxide	45	1.9	7.8	4.0	1.8
Propylene carbonate	63	2.6	10	6	2.6

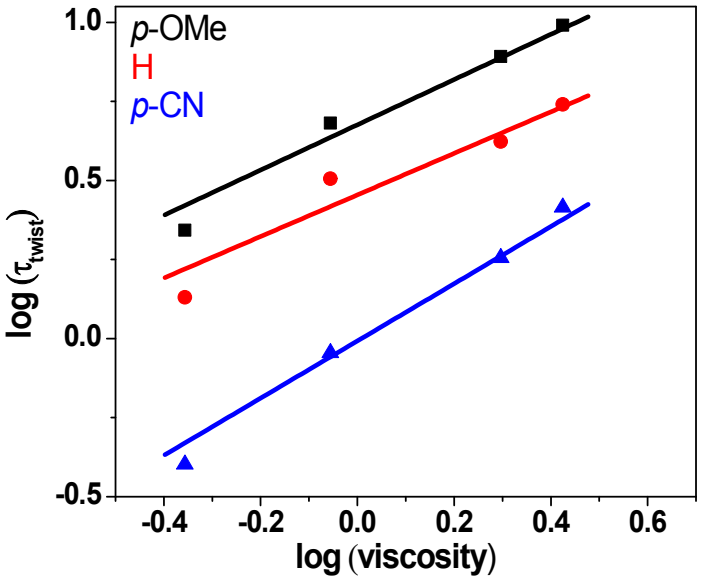


Figure S4: log-log plot of the twisting time versus viscosity of three DMAC derivatives.