Supporting Information

Two-State Intramolecular Charge Transfer (ICT) with 3,5-Dimethyl-4-(Dimethylamino)benzonitrile (MMD) and Its Meta-Isomer mMMD. Ground State Amino Twist Not Essential for ICT

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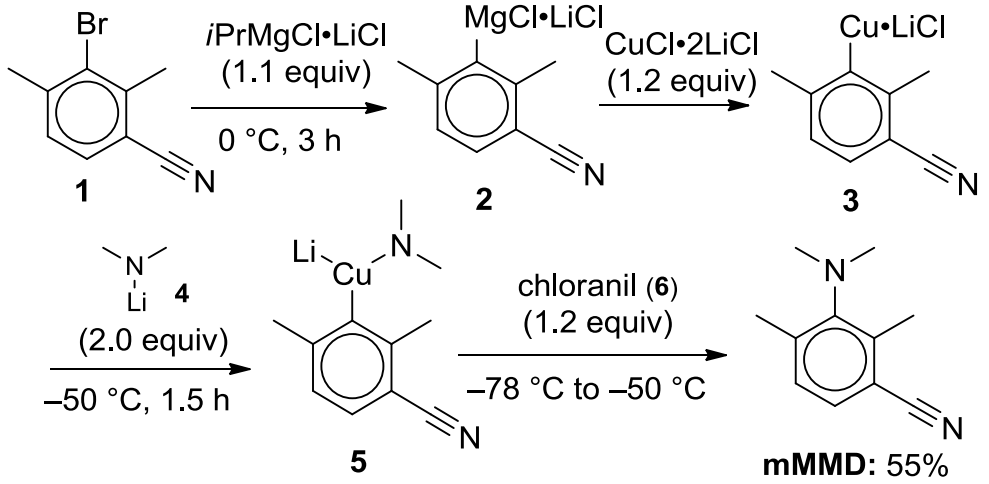
CCDC Numbers for the crystal structures:

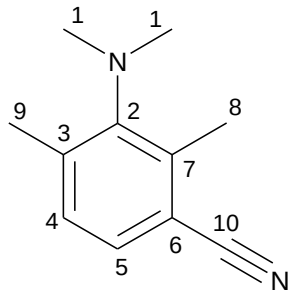
CBQ: 1423222; DTABN: 1427925; mMMD: 1423148.

Synthesis Procedure[1] of 2,4-dimethyl-3-(dimethylamino)benzonitrile (mMMD)



i-PrMgCl•LiCl (0.79 mL, 1.1 mmol, 1.39 M in THF) was cooled to 0 °C and 3-Bromo-2,4-dimethylbenzonitrile **1** (210 mg, 1.0 mmol) was added. The mixture was stirred at 0 °C for 3 h to produce the Grignard reagent **2**. The Br/Mg-exchange was completed after 3 h as determined by GC-analysis of reaction aliquots. CuCl•2LiCl (1.2 mL, 1.2 mmol, 1.0 M in THF) was added to the Grignard reagent **2** at –50 °C and the mixture was stirred for 45 min. To the resulting arylcopper reagent **3,** the *N*-lithium dimethylamide **4** (2.0 mmol; prepared by adding *n*-BuLi (2.0 mmol) to a 1.0 M of dimethylamine in THF (2.0 mL, 2 mmol) at –78 °C in THF, stirring the mixture for 20 min at –78 °C and then 15 min at 0 °C) was added dropwise and the mixture was further stirred for 90 min at –50 °C. The reaction mixture was cooled to –78 °C, then a solution of chloranil **6** (295 mg, 1.2 mmol) in anhydrous THF (7 mL) was added slowly over a period of 45 min. The mixture was allowed to warm up to –50°C and was further stirred for 12 h. Diethyl ether (DEE, 10 mL) was added to the crude reaction mixture, which was then filtered through *Celite* and the residue was thoroughly washed with DEE (ca. 150 mL). The filtrate (organic phase) was washed with NH_4OH (aq., 2.0 M, 2 x 20 mL) and the combined aqueous phases were extracted with DEE. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography using gradient increase of DEE in *n*-pentane gave **mMMD** (97 mg, 55 %).

(1) del Amo, V.; Dubbaka, S. R.; Krasovskiy, A.; Knochel, P. General Preparation of Primary, Secondary and Tertiary Arylamines via the Oxidative Coupling of Polyfunctional Aryl and Heteroaryl Amidocuprates *Angew. Chem., Int. Ed.* **2006**, *45*, 7838-7842.



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, ^{3}J(H,H) = 7.9 Hz, 1H, H5), 7.06 (d, ^{3}J(H,H) = 7.9 Hz, 1H, H4), 2.83 (s, 6H, H1), 2.50 (s, 3H, H9), 2.35 (s, 3H, H8).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 150.4 (C2), 143.3 (C7), 141.2 (C3), 129.4 (C4), 128.9 (C5), 118.8 (C10), 111.7 (C6), 42.2 (C1), 19.6 (C9), 17.2 (C8).

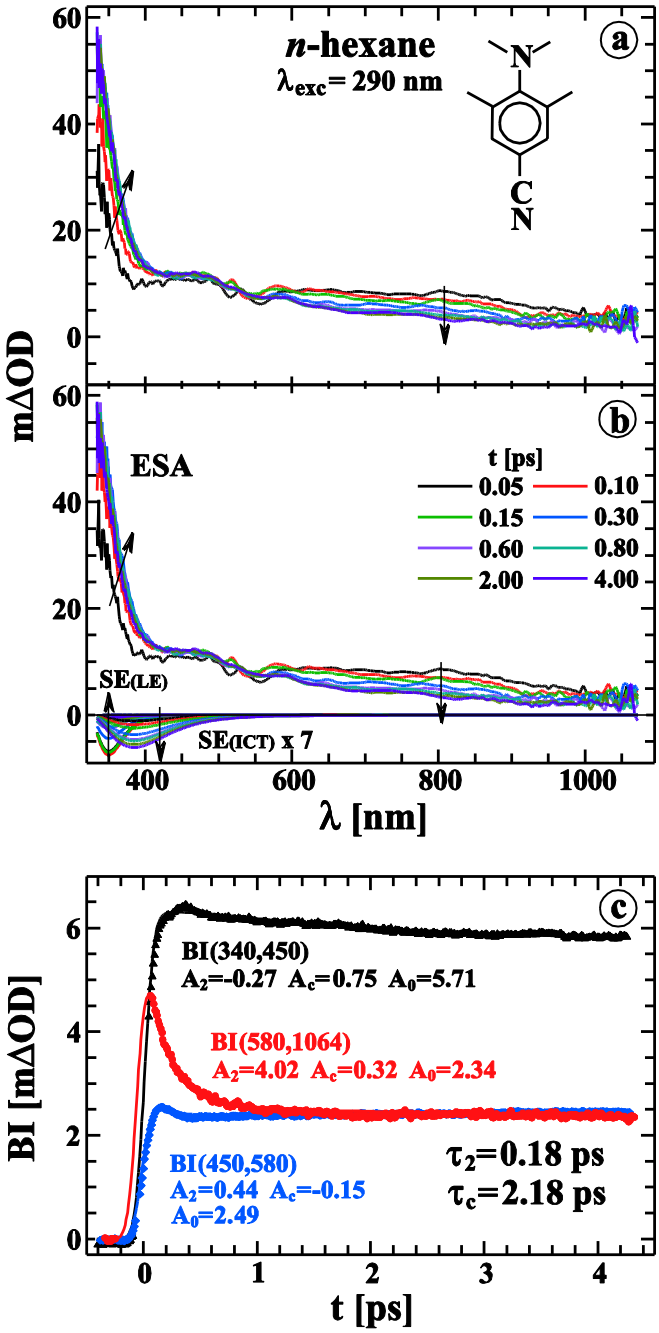


Figure S1. MMD in *n*-hexane at 290 nm excitation (spectral range: 335-1070 nm). (a) Transient absorption spectra and (b) excited state absorption (ESA) spectra after correction for bleaching (BL) and stimulated emission (SE), at eight pump-probe delay times between 0.05 and 4.0 ps. The BL and SE (LE + ICT, cf Figure 2a) spectra are also depicted. A growing-in around 400 nm and a decay around 800 nm is observed, indicated by arrows. (c) For the band integral BI(340,450), between 400 and 500 nm in the ESA spectrum, a growing-in (negative amplitude A_2) with a time τ_2 = 0.18 ps is determined. For BI(580,1064) and BI(450,580) a decay with the same τ_2 = 0.18 ps is obtained. For all BIs, an additional time τ_C = 2.18 ps is found, see text. The times result from a simultaneous analysis of the BIs. The amplitudes are A_2 and A_c, the offset is A_0 (eqs 4 and 5). mΔOD is the optical density/1000.

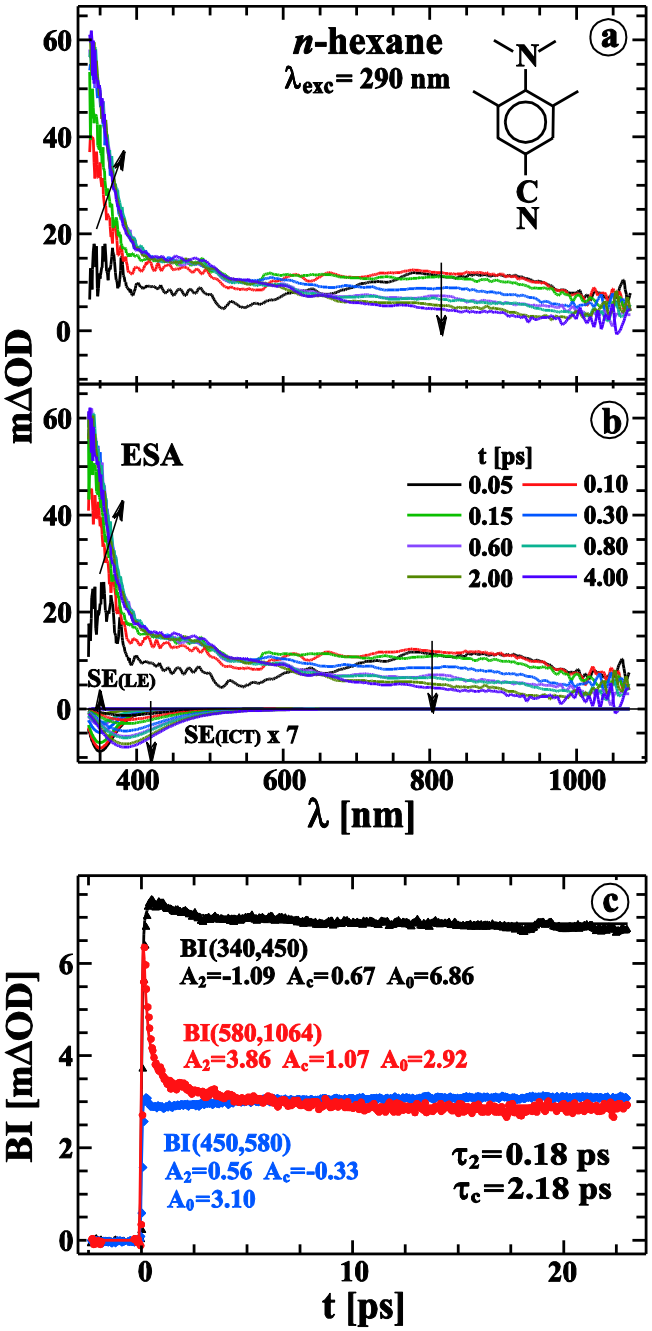


Figure S2. MMD in *n*-hexane at 290 nm excitation (spectral range: 334-1072 nm). (a) Transient absorption spectra and (b) excited state absorption (ESA) spectra, at eight pump-probe delay times between 0.05 and 4.0 ps, after correction for bleaching (BL) and stimulated emission (SE). The BL and SE (LE + ICT, cf Figure 2a) spectra are also depicted. A growing-in around 400 nm and a decay around 800 nm is observed, indicated by arrows. (c) For the band integral BI(340,450), between 400 and 500 nm in the ESA spectrum, a growing-in (negative amplitude A_2) with a time τ_2 = 0.18 ps is determined. For BI(580,1064) and BI(450,580) a decay with the same τ_2 = 0.18 ps is found. For all BIs, an additional time τ_C = 2.18 ps is obtained, see text. The times result from a simultaneous analysis of the BIs. The amplitudes are A_2 and A_c, the offset is A_0 (eqs 4 and 5). mΔOD is the optical density/1000.

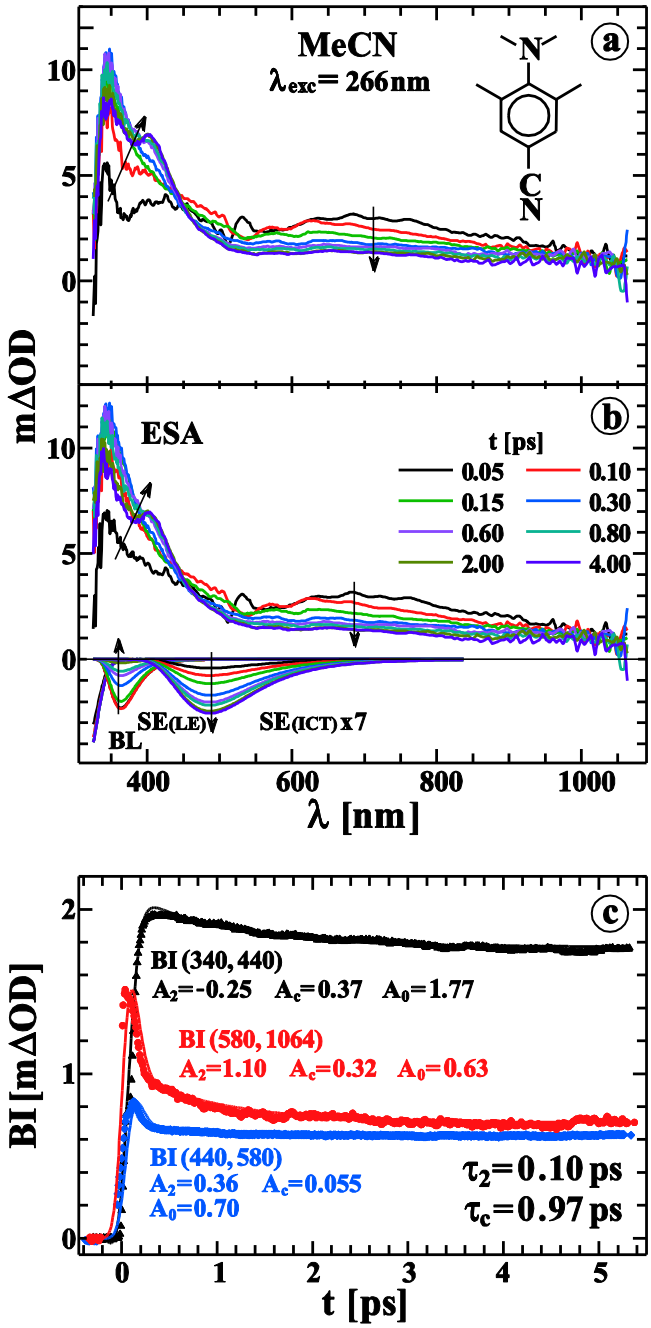


Figure S3. MMD in acetonitrile (MeCN) at 266 nm excitation (spectral range: 334-1072). (a) Transient absorption spectra and (b) excited state absorption (ESA) spectra after correction for bleaching (BL) and stimulated emission (SE), at eight pump-probe delay times between 0.05 and 4.0 ps,. The BL and SE (ICT, cf Figure 2b) spectra are also depicted. A growing-in around 420 nm and a decay around 700 nm is observed, indicated by arrows. (c) For the band integral BI(340,440), between 340 and 440 nm in the ESA spectrum, a growing-in (negative amplitude A_2) with a time τ_2 = 0.10 ps is determined. For BI(580,1064) and BI(440,580) a decay with the same τ_2 = 0.10 ps is obtained. For all BIs, an additional time τ_C = 0.97 ps is found, see text. The times result from a simultaneous analysis of the BIs. The amplitudes are A_2 and A_c, the offset is A_0 (eqs 4 and 5). mΔOD is the optical density/1000.

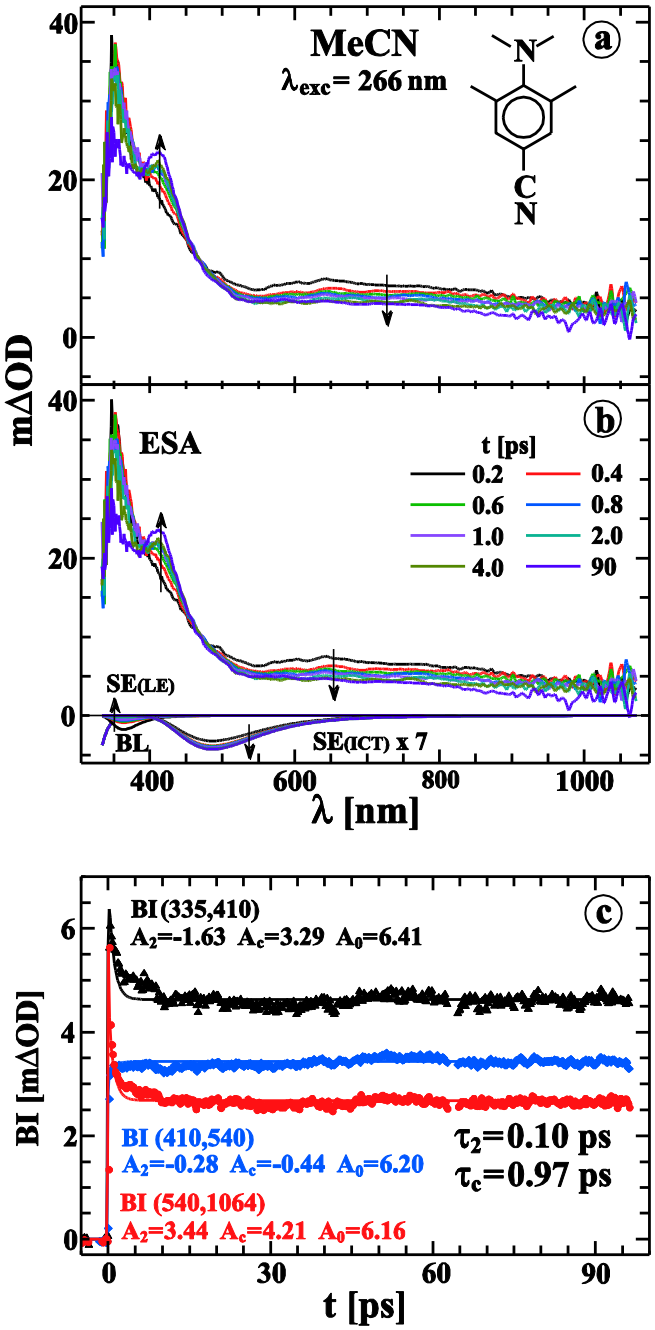


Figure S4. MMD in acetonitrile (MeCN) at 266 nm excitation (spectral range: 334-1072). (a) Transient absorption spectra and (b) excited state absorption (ESA) spectra, at eight pump-probe delay times between 0.05 and 4.0 ps, after correction for bleaching (BL) and stimulated emission (SE). The BL and SE (ICT, cf Figure 2b) spectra are also depicted. A growing-in around 420 nm and a decay around 640 nm is observed, indicated by arrows. (c) For the band integral BI(335,410), between 340 and 440 nm in the ESA spectrum, as well as for BI(335,410), a growing-in (negative amplitude A_2) with a time τ_2 = 0.10 ps is determined. For BI(580,1064) and BI(410,540) a decay with the same τ_2 = 0.10 ps is found. For all BIs, an additional time τ_C = 0.97 ps is obtained, see text. The times result from a simultaneous analysis of the BIs. The amplitudes are A_2 and A_c, the offset is A_0 (eqs 4 and 5). mΔOD is the optical density/1000.

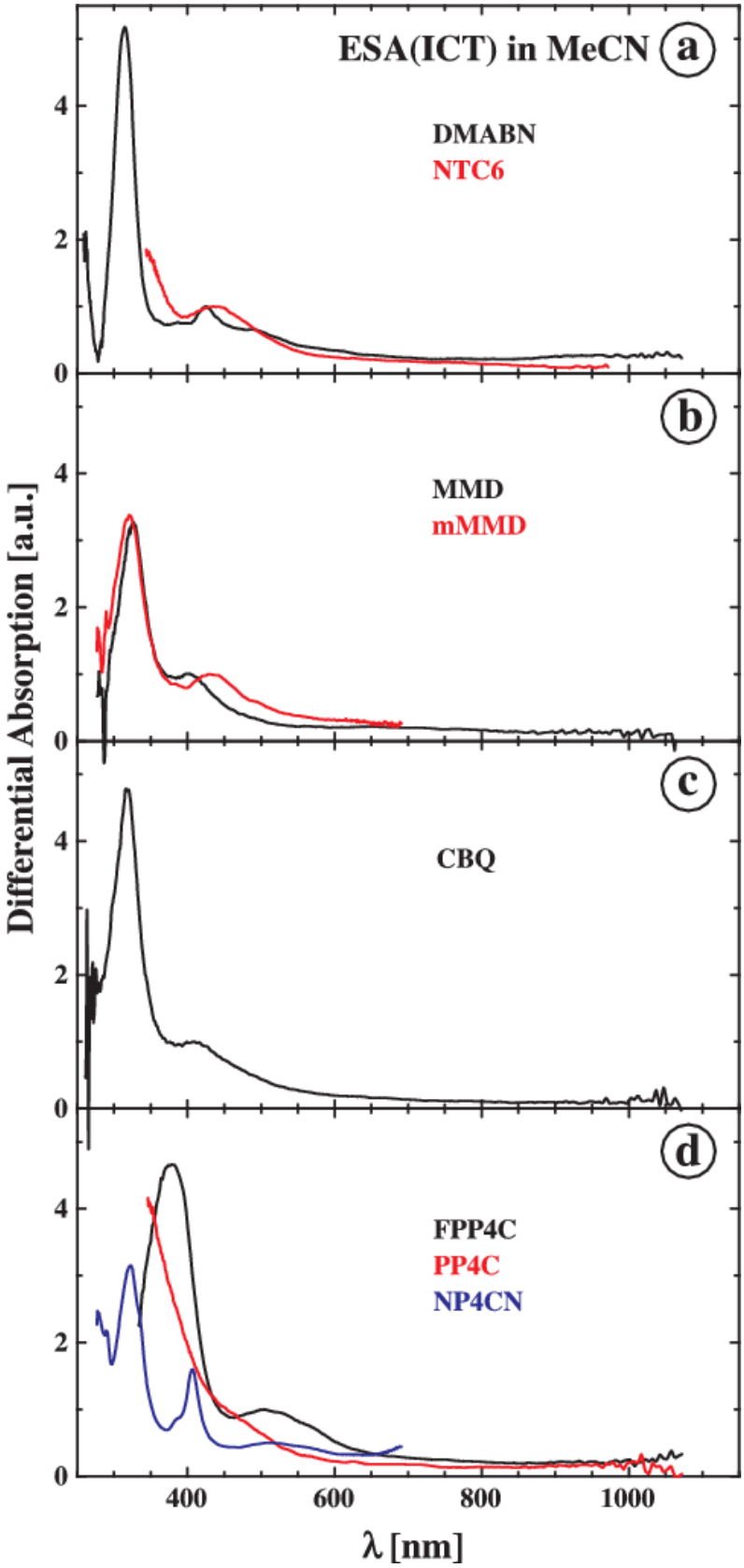


Figure S5. ICT Excited state absorption (ESA) spectra in acetonitrile (MeCN) of (a) 4-(dimethylamino)benzonitrile (DMABN) and 1-*tert*-butyl-6-cyano-1,2,3,4-tetrahydroquinoline (NTC6), (b) 3,5-dimethyl-4-(dimethylamino)benzonitrile (MMD) and 2,4-dimethyl-3-(dimethylamino)benzonitrile (mMMD), (c) CBQ, and (d) 4-cyanofluorazene (FPP4C), 4-cyano-*N*-phenylpyrrole (PP4C) and *N*-(4-cyanophenyl)carbazole (NP4CN). mΔOD is the change in optical density/1000. DMABN: ref 24. NTC6: ref 20. CBQ: ref n. FPP4C and PP4C: *J. Phys. Chem. A* **2008**, *112*, 8238-8253. NP4CN: ref 62.

Table S1. Data for the Dielectric Constant and Refractive Index and the Polarity Parameter $f(\varepsilon) - \frac{1}{2}f(n^2)$ (Eqs 2 and 3) for a Series of Solvents Spanning the Polarity Scale

Solvent	ε	n	$f(\varepsilon) - \frac{1}{2}f(n^2)$
pFMCH[a] (1)	1.82	1.279	0.102
n-pentane (2)	1.83	1.355	0.089
3-methylpentane (3)	1.88	1.374	0.092
n-hexane (4)	1.88	1.372	0.092
n-hexadecane (5)	2.05	1.435	0.102
toluene (6)	2.37	1.493	0.126
di(*n*-pentyl) ether (7)	2.86	1.412	0.177
di(*n*-butyl) ether (8)	3.05	1.397	0.192
di(n-propyl) ether (9)	3.26	1.379	0.207
diethyl ether (10)	4.24	1.350	0.253
ethyl acetate (11)	5.99	1.370	0.292
tetrahydrofuran (12)	7.39	1.405	0.307
n-butyl cyanide (13)	19.8	1.395	0.366
n-propyl cyanide (14)	24.2	1.382	0.375
ethyl cyanide (15)	29.2	1.363	0.384
acetonitrile (16)	36.7	1.342	0.393

[a]Perfluoromethylcyclohexane.

Table S2. DecayTimes τ_2 and τ_1 and Amplitude Ratios *A* of Double Exponential Picosecond Fluorescence Decays (eqs 6-8), ICT Rate Constants k_a and k_d, ICT and LE Lifetimes τ'_0(ICT) and τ_0(LE) (eqs 9-15), with the ICT Reaction Enthalpy -Δ*H*

D/A-molecule	solvent	T [°C]	τ_2 [ns]	τ_1 [ns]	*A*	τ_0 [ns]	$1/\tau_2$ [$10^{10}s^{-1}$]	k_a [$10^{10}s^{-1}$]	k_d [$10^{10}s^{-1}$]	τ'_0(ICT) [ns]	k_a/k_d	-*ΔH* [kJ/mol]
DMABN[a,b]	toluene	-90	0.297	3.92	2.40	3.61	0.337	0.23	0.088	3.88	2.61	5.9
DMABN[a,c]	DEE[d]	20	0.025	3.28	1.32	3.91	4.0	2.26	1.71	3.91	1.32	15
DMABN[a,e]	MeCN[f]	25	0.0041	3.80	516	3.41	24.4	24.0	0.047	3.80	511	27
DMABN[a,e]	MeCN[f]	-45	0.0076	3.53	14470	3.72	13.11	12.08	0.0009	3.53	14533	27
DPrABN[g,h]	toluene	20	0.018	2.76	9.5	3.65	5.56	5.0	0.53	2.70	9.4	15
DPrABN[i,h]	toluene	-20	0.037	2.87	22.4	3.87	2.70	2.56	0.14	2.80	23.1	15
DPrABN[e,c]	DEE	20	0.013	2.84	11.72	3.91	7.69	7.07	0.60	3.91	11.78	
DIABN[g,h]	*n*-hexane	25.5	0.003	0.94	>430	3.42	33.3	34	<0.08	0.94	>425	
DIABN[g,h]	*n*-hexane	-90	0.012	0.79	>210	4.10	8.3	8	<0.04	0.79	>200	
M4D[i,h]	DEE	20	0.002	0.711	1593	3.91	50.0	49.9	0.031	0.711	1599	
NTC6[j,k]	*n*-hexane	25	0.0021	2.44	0.43	3.0	47.6	14.3	33.3	1.7	0.43	
NTC6[j,l]	*n*-hexane	-95	0.020	3.99	1.08	3.06	5.0	2.6	2.4	5.6	1.08	
NTC6[j,k]	DEE	-70	0.007	8.54	21.9	3.09	14.3	13.6	0.62	9.29	21.9	
FPP[m,d]	MeCN[f]	-45	0.0036	15.36	24.4	11.66	27.78	27.0	1.09	15.57	24.8	
NP4C[n,o]	*n*-hexane	-75	0.0155	4.19	0.38	4.5		1.8	4.7	3.55	0.38	
NP4C[n,o]	*n*-hexane	-95	0.0247	4.04	0.77	4.5		1.7	2.3	3.57	0.77	
CVL[p,q]	MeCN[f]	75	0.0081	1.58	10.7	39	12.3	11.4	1.06	1.45	10.8	19.7
CVL[p,q]	MeCN	-45	0.0155	0.84	273	39	6.5	6.4	0.023	0.84	280	19.7
2Py(3)2Py[r]	MCH[s]	25	7.56	151.5	94	367	0.0132	0.0128	0.00013	150	98.5	

[a]4-(Dimethylamino)benzonitrile. [b]Ref 5. [c]Ref 18. [d]Diethyl ether. [e]Ref 24. [f]Acetonitrile. [g]4-(Di-*n*-propylamino)benzonitrile. [h]Ref 23. [i]4-(Diisopropylamino)benzonitrile. [h]Ref 21. [i]4-(*N*-azetidinyl)-3,5-dimethylbenzonitrile. [j]1-*Tert*-butyl-6-cyano-1,2,3,4-tetrahydroquinoline. [k]Ref 20. [l]Ref 19. [m]Fluorazene. [n]*N*-(4-cyanophenyl)carbazole. [o]Ref 62. [p]Crystal Violet Lactone. [q]*J. Phys. Chem. A* **2013**, *117*, 7721-7736. [r]1,3-Di-(2-pyrenyl)propane, see Ref. 71. [s]Methylcyclohexane.

Table S3. Ratio of the LE and ICT Radiative Rate ConstantsDecayTimes k_f(LE)/k'_f(ICT) for Aminobenzonitriles

D/A molecule	solvent	T[°C]	k_f(LE)/k'_f(ICT)	k_f(LE) [10^9 s^{-1}]	k'_f(ICT) [10^9 s^{-1}]	Ref
DMABN[a]	MeCN[b]	25	8.2	0.065	0.0079	ref 24
DMABN[a]	MeCN[b]	-45	12.5	0.073	0.0058	ref 24
DIABN[d]	*n*-hexane	25.5	6.7	0.06	0.009	ref 51
DIABN[d]	*n*-hexane	-90.3	6.7	0.04	0.006	ref 51
CVL[e,f]	MeCN	25	1.5			
NTC6[g]	*n*-hexane	25	1.2	0.093	0.076	ref 20
NTC6[g]	*n*-hexane	25	1.1	0.089	0.080	ref 20
NTC6[g]	*n*-hexane	-95	1.3	0.11	0.082	ref 20
NTC6[g]	*n*-hexane	-95	1.3	0.10	0.076	ref 20
NTC6[g]	DEE[c]	-70	2.2	0.13	0.059	ref 19
PP[h,j]	PrCN[i]	-45	2.8			
MDB[k]	toluene	25	3.3	0.070	0.021	ref 23
EDB[l]	toluene	25	3.7	0.070	0.019	ref 23
PrDB[m]	toluene	25	2.1	0.055	0.026	ref 23
DMABN[a]	toluene	25	3.0	0.057	0.019	ref 23
DEABN[o]	toluene	25	3.9	0.062	0.016	ref 23
DPrABN[p]	toluene	25	2.0	0.040	0.020	ref 23

[a]4-(Dimethylamino)benzonitrile. [b]MeCN: acetonitrile. [c]Diethyl ether. [d]4-(Diisopropylamino)benzonitrile. [e]Crystal Violet Lactone. [f]*J. Phys. Chem. A* **2013**, *117*, 7721-7736. [g]1-*Tert*-butyl-6-cyano-1,2,3,4-tetrahydroquinoline (NTC6). [h]*N*-Phenylpyrrole. [i]*n*-Propylcyanide. [j]*J. Phys. Chem. A* **2006**, *110*, 12760-12768. [k]4-Dimethylamino-2,6-dimethyl-benzonitrile. [l]4-Diethylamino-2,6-dimethyl-benzonitrile. [m]4-Di-*n*-propylamino-2,6-dimethyl-benzonitrile. [o]4-(Diethylamino)benzonitrile. [p]4-(Di-*n*-propylamino)benzonitrile.

Table S4. Decay Times τ_2 from Femtosecond Transient Absorption Spectra (Eqs 4 and 5) at 22 °C. DecayTimes τ_1 from Single Exponential Picosecond Fluorescence Decays (Eqs 6-8), ICT Rate Constants k_a and k_d, ICT and LE Lifetimes τ'_0(ICT), τ_0(LE) (Scheme 1), and Fluorescence Quantum Yield Ratios Φ(LE)/Φ'(ICT) (Eq 16) at 25 °C for MMD in *n*-hexane. Variation of τ_0(LE) and k_f/k'_f. See Table 8

τ_2 [ps]	τ_1 [ns]	τ_0 [ns]	Φ(LE)/ Φ'(ICT)	$1/\tau_2$ [$10^{10}s^{-1}$]	$1/\tau_1$ [$10^{10}s^{-1}$]	k_a [$10^{10}s^{-1}$]	k_d [$10^{10}s^{-1}$]	τ'_o(ICT)[a] [ns]	k_a/k_d	k_f/k'_f
0.18	1.17	3.4	0.078	555	0.0855	549.7	5.3	1.17	103.7	8
0.18	1.17	1.0	0.078	555	0.0855	549.6	5.3	1.17	103.7	8
0.18	1.17	3.4	0.078	555	0.0855	547.9	7.0	1.17	78.3	6
0.18	1.17	3.4	0.078	555	0.0855	544.4	10.5	1.17	51.8	4
0.18	1.17	3.4	0.078	555	0.0855	531.0	14.0	1.17	37.9	3
0.18	1.17	3.4	0.078	555	0.0855	524.2	20.8	1.17	25.2	2
0.18	1.17	3.4	0.078	555	0.0855	514.9	40.1	1.17	12.8	1

[a]Approximate value, see text.