Supporting Information

for

Dual Fluorescence and Ultrafast Intramolecular Charge Transfer with 6-*N*,*N*-Dialkylaminopurines. A Two State Model

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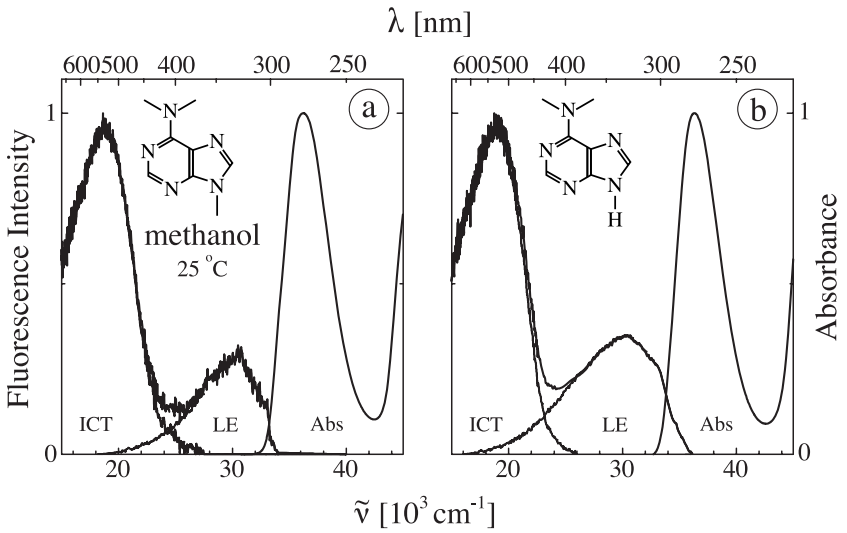

Figure S1. Fluorescence (ICT and LE) and absorption (Abs) spectra of (a) DMPURM and (b) DMPURH in methanol at 25 °C, see Tables 1 and 2.

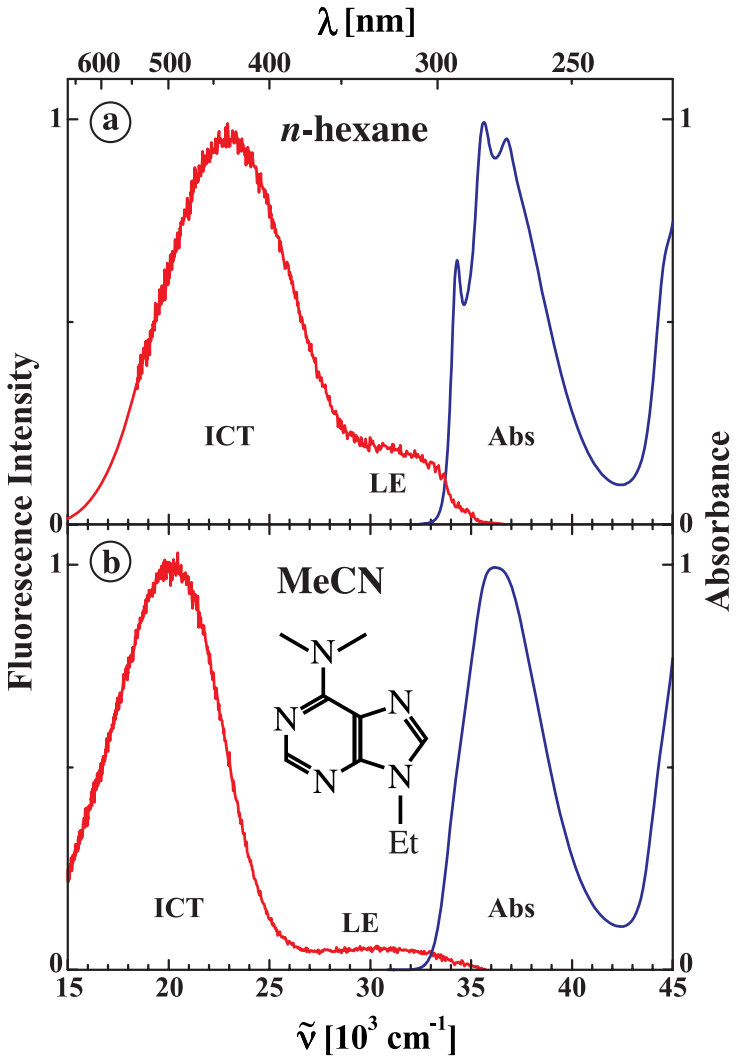

Figure S2. Fluorescence (ICT and LE) and absorption (Abs) spectra of DMPURE in (a) *n*-hexane and (b) MeCN at 25 °C, see Table S1.

Table S1: Data Obtained from the Fluorescence and Absorption Spectra of DMPURE and DMPURM (Table 1) in *n*-Hexane and MeCN at 25 °C[a]

	DMPURE		DMPURM	
solvent	*n*-hexane	MeCN	*n*-hexane	MeCN
Φ(fl)	0.0026	0.004	0.0032	0.0034
$\tilde{\nu}^{max}$ (S_1,abs) 0-0 [cm^{-1}]	34300		34280	
$\tilde{\nu}^{max}$ (S_2,abs) [cm^{-1}]	35640	36185	35610	36300
$\tilde{\nu}^{max}$ (LE) [cm^{-1}]	31170	30275	30530	29850
$\tilde{\nu}^{max}$ (fl) [cm^{-1}] $\tilde{\nu}^{max}$ (ICT) [cm^{-1}]	22970 (22850)	20130	23140 (23100)	20410
Φ´(ICT)/Φ(LE)	5.3	18	5.0	20

[a] See footnotes in Table 1.

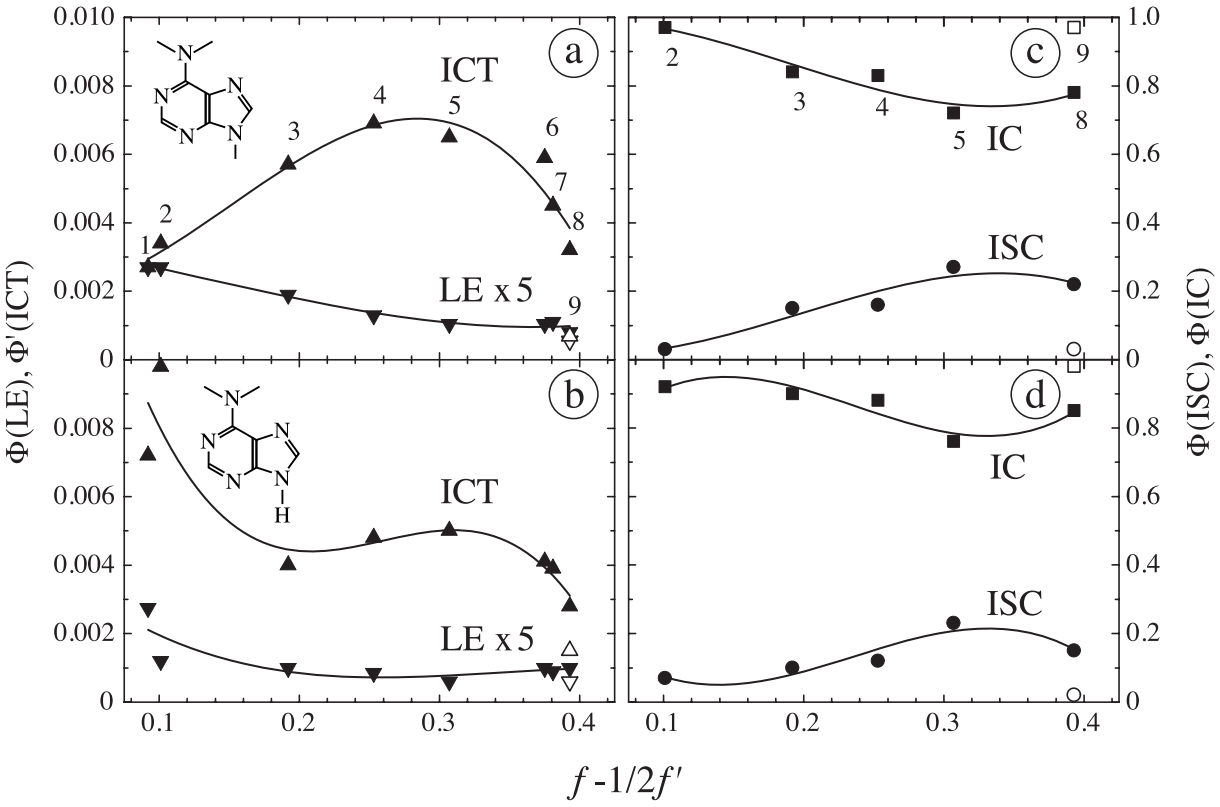

Figure S3. The yields Φ´(ICT), Φ(LE), Φ(IC), and Φ(ISC) of DMPURM (a and c) and DMPURH (b and d), as a function of the solvent polarity parameter $f(\varepsilon) - \frac{1}{2}f(n^2)$ (eqs 2 and 3). Solvents: 1: *n*-hexane; 2: cyclohexane; 3: di-*n*-butyl ether; 4: diethyl ether; 5: tetrahydrofuran; 6: *n*-propyl cyanide; 7: ethyl cyanide; 8: MeCN; 9: methanol. See Tables 1 and 2.

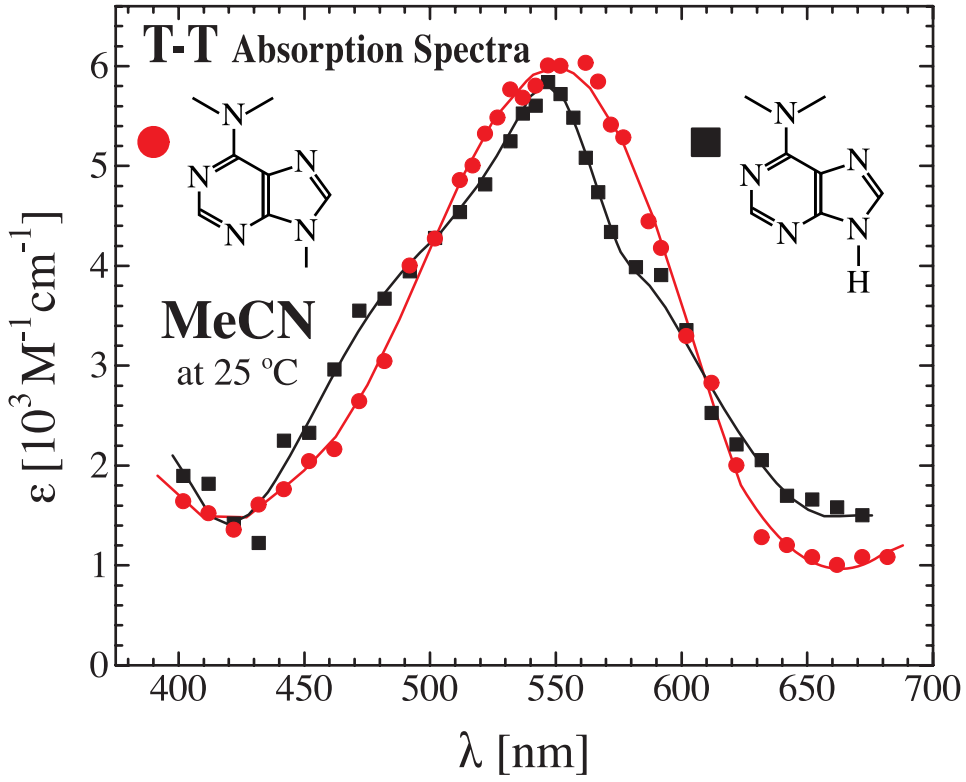

Figure S4. Triplet-triplet absorption spectra of DMPURM (red) and DMPURH (black) in MeCN at 25 °C. The absorption maximum of DMPURM is at 550 nm (ε^{max} = 6000 $M^{-1}cm^{-1}$), that of DMPURH at 545 nm (ε^{max} = 5800 $M^{-1}cm^{-1}$).

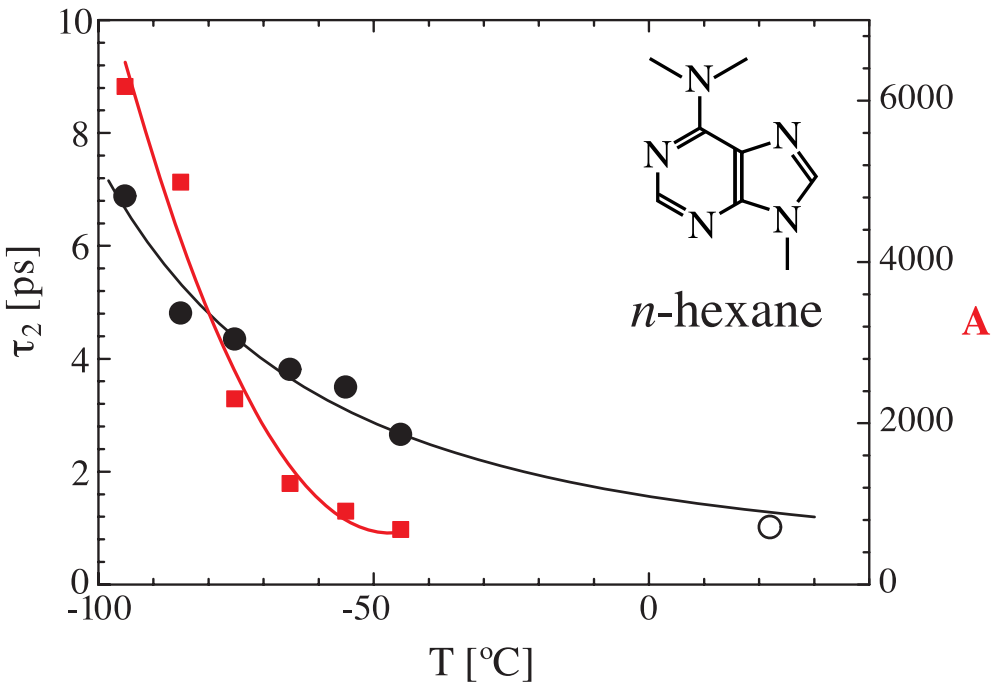

Figure S5. Plot of τ_2(LE) (eq 8) and the amplitude ratio $A = A_{12}/A_{11}$ (eq 10) for DMPURM in *n*-hexane as a function of temperature, see Figure 14. The ESA decay time of 1.0 ps at 22 °C is for CHX.

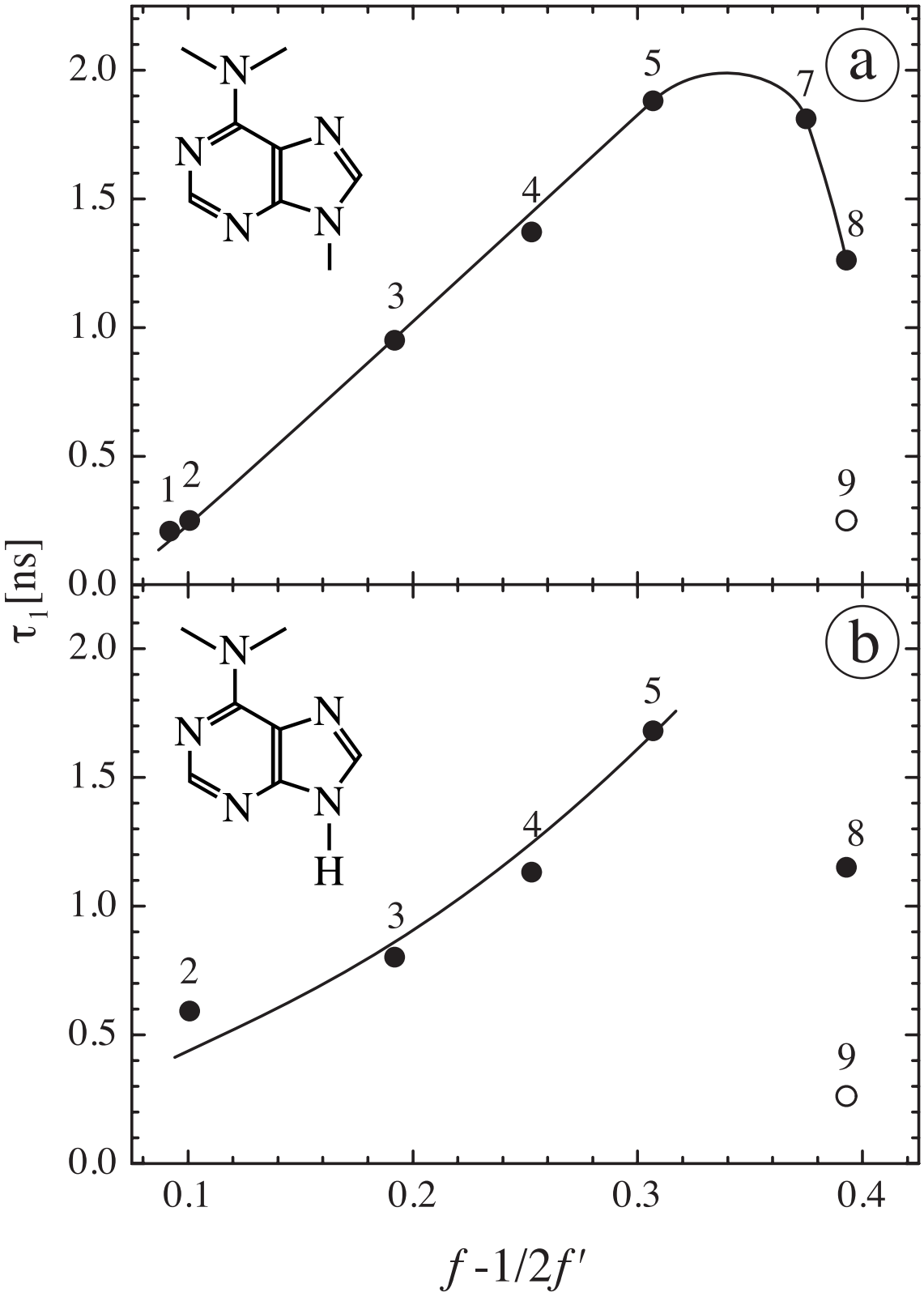

Figure S6. The long decay time τ_1(ICT) of (a) DMPURM and (b) DMPURH as a function of the solvent polarity parameter $f(\varepsilon) - \frac{1}{2}f(n^2)$ (eqs 2 and 3). Solvents: 1: *n*-hexane; 2: cyclohexane; 3: di-*n*-butyl ether; 4: diethyl ether; 5: tetrahydrofuran; 6: *n*-propyl cyanide; 8: MeCN; 9: methanol. See Tables 1, 2, and 4.

TABLE S2: Absorption Maxima $\tilde{\nu}^{max}$ (S_1,abs) and $\tilde{\nu}^{max}$ (S_2,abs), the ICT and LE Fluorescence Maxima $\tilde{\nu}^{max}$ (ICT) and $\tilde{\nu}^{max}$ (LE), the Fluorescence Quantum Yield Ratios Φ´(ICT)/Φ(LE), the Singlet Energies $E(S_1)$, and the Energy Gaps $\Delta E(S_1,S_2)$ for a Series of Adenines at 25 °C[a]

	$\tilde{\nu}^{max}$ (S_1,abs) [cm^{-1}]	$\tilde{\nu}^{max}$ (S_2,abs) [cm^{-1}]		$\tilde{\nu}^{max}$ (ICT) [cm^{-1}]		$\tilde{\nu}^{max}$ (LE) [cm^{-1}]		Φ´(ICT)/Φ(LE)		$E(S_1)$[b] [cm^{-1}]		$\Delta E(S_1,S_2)$ [cm^{-1}]	
solvent	*n*-hexane	*n*-hexane	MeCN	*n*-hexane	MeCN	*n*-hexane	MeCN	*n*-hexane	MeCN	*n*-hexane	MeCN	*n*-hexane	MeCN
DMPURM	34280	35610	36300	23140	20410	30530	29850	5.0	20	34000	33600	1610	2700
DEPURM	34060	35370	35890	23920	20720			25	51	33800	33420	1570	2470
DPrPURM	33940	35240	35790	24170	21060			23	49	33675	33260	1565	2530
DPePURM		-	35800	-	20950			-	15		33100		2700
DMPURE	34300	35640	36185	22970	20130	31170	30275	5.3	18	34080	33605	1558	2580
MPURM	35490	37920	37650	-[c]	-	-	-	-	-	35225	34670	2695	2980
PURM		38970	38690	-	-	-	-	-	-	36540	35870	2430	2820
DMPURH	34450	35730	36500	22680	20360	31180	29580	13	14	33930	33860	1800	2640

[a] See footnotes in Table 1. [b] Estimated relative to the value of DMPURM, taking into account the shift of the absorption spectrum. [c] Only impurity fluorescence, see the text (Figure 16).

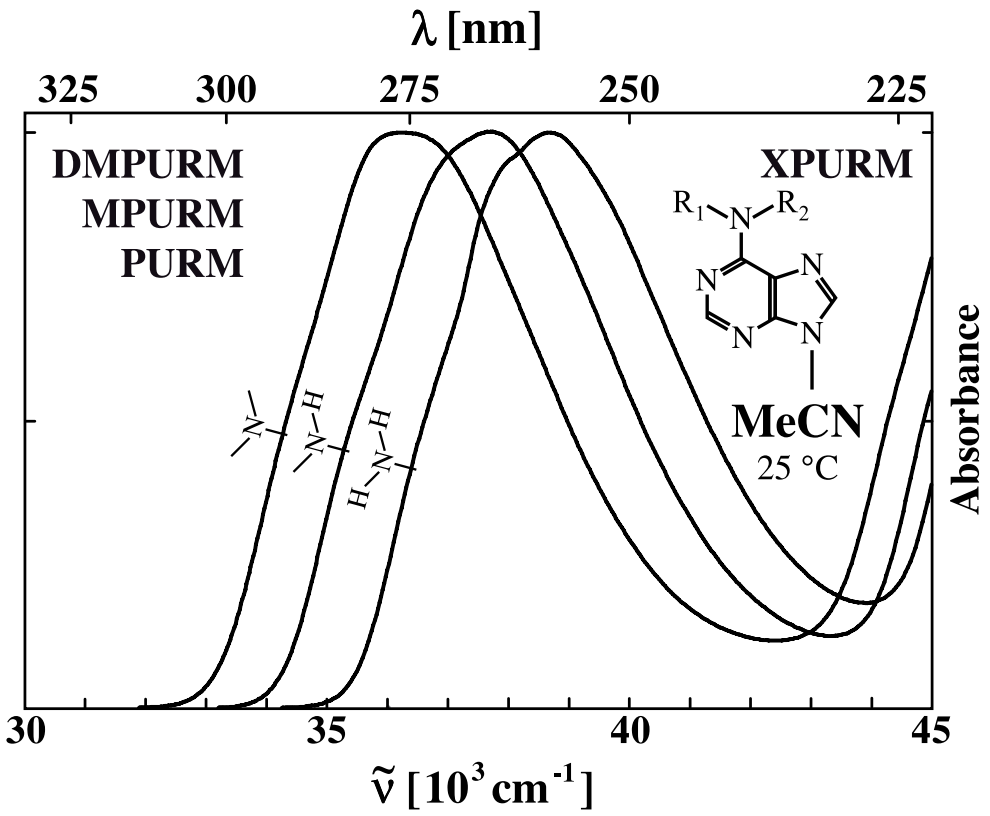

Figure S7. Absorption spectra of DMPURM, MPURM, and PURM in MeCN at 25 ^{o}C.