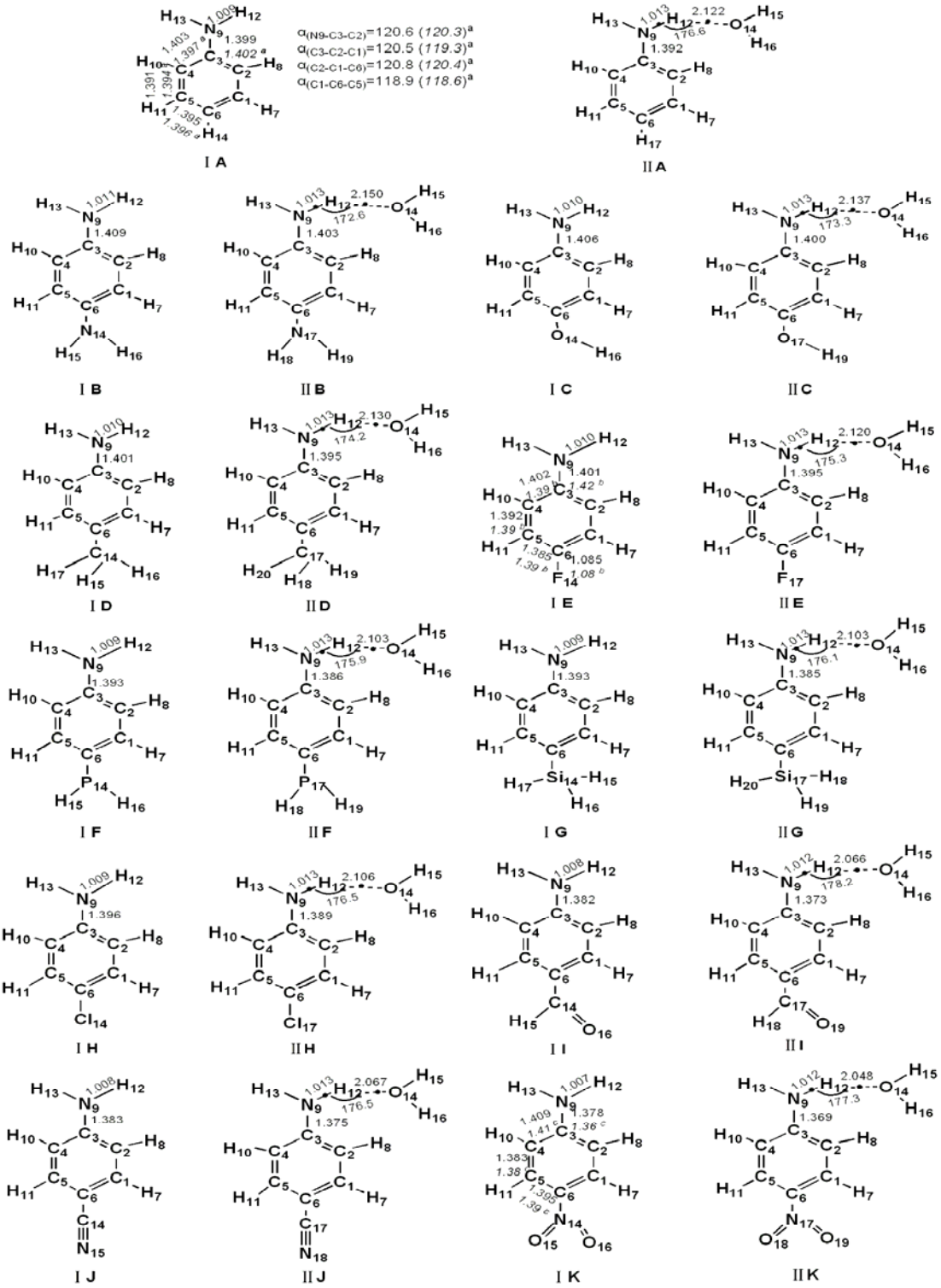

Fig. S1. Geometries of isolated aniline derivatives (Ⅰ A~ Ⅰ K) and corresponding hydrated complexes (Ⅱ A~ Ⅱ K) calculated at the B3LYP/6-311++G(d,p) level of theory (bond length in Å and angle in degree; the *italics* indicate experimental data; the black dots indicate bond critical points).

Table S1 The C–N Bond Lengths ($R_{C–N}$) and Proton Donating N–H Bond Lengths ($R_{N–H}$) and Stretching Frequencies ($\nu_{N–H}$) in all *para*-substituted Aniline Monomers (Ⅰ) and All Corresponding Monohydrated Complexes (Ⅱ) and Variations of N–H Bond Lengths ($\Delta R_{N–H}$) and C–N Bond lengths ($\Delta R_{C–N}$) and N-H Stretching Frequencies ($\nu_{N–H}$) and Corresponding Red Shifts of Frequencies ($\Delta\nu_{N–H}$) upon Formation of the Complex, Calculated at the B3LYP/6-311++G(d, p) Level of Theory and Some Experimental Values of Frequencies in Brackets

X	Bond Length, Å						Stretching Frequency, cm^{-1}					
	$R_{C–N}$		$\Delta R_{C–N}$[a]	$R_{N–H}$		$\Delta R_{N–H}$[b]	$\nu_{as\ N–H}$		$\Delta\nu_{as\ N–H}$[c]	$\nu_{s\ N–H}$		$\Delta\nu_{s\ N–H}$[d]
	Ⅰ	Ⅱ	Ⅱ – Ⅰ	Ⅰ	Ⅱ	Ⅱ – Ⅰ	Ⅰ	Ⅱ	Ⅱ – Ⅰ	Ⅰ	Ⅱ	Ⅱ – Ⅰ
NH_2	1.4087	1.4030	-0.0057	1.0105	1.0134	0.0029	3644.4	3635.7	-8.7	3551.8	3529.7	-22.1
OH	1.4059	1.4002	-0.0057	1.0101	1.0132	0.0031	3651.1	3642.0	-9.1	3557.7	3532.8	-24.9
CH_3	1.4011	1.3946	-0.0065	1.0096	1.0128	0.0032	3659.9	3649.6	-10.3	3563.9	3536.2	-27.7
H	1.3986	1.3915	-0.0071	1.0093	1.0128	0.0035	3666.1	3654.8	-11.3	3568.6	3532.0	-36.6
							(3508.2)[e]	(3485.0)[f]	-23.2	(3421.8)[e]	(3383.0)[f]	-38.8
F	1.4008	1.3945	-0.0063	1.0095	1.0129	0.0034	3661.9	3651.4	-10.5	3566.4	3536.0	-30.4
PH_2	1.3931	1.3855	-0.0076	1.0088	1.0126	0.0038	3673.8	3662.6	-11.2	3574.3	3538.8	-35.5
SiH_3	1.3928	1.3852	-0.0076	1.0088	1.0126	0.0038	3674.5	3662.9	-11.6	3574.5	3539.2	-35.3
Cl	1.3962	1.3894	-0.0068	1.0090	1.0128	0.0038	3669.4	3657.5	-11.9	3571.7	3536.6	-35.1
CHO	1.3816	1.3727	-0.0089	1.0077	1.0123	0.0046	3694.3	3681.6	-12.7	3588.7	3540.0	-48.7
CN	1.3834	1.3752	-0.0082	1.0079	1.0125	0.0046	3691.1	3677.8	-13.3	3587.1	3538.3	-48.8
							(3538.0)[g]	(3532.0)[g]	-6.0	(3445.0)[g]	(3420.0)[g]	-25.0
NO_2	1.3776	1.3685	-0.0091	1.0073	1.0124	0.0051	3701.7	3687.9	-13.8	3594.5	3537.8	-56.7
							(3510.0)[h]	(3477.0)[h]	-33.0	(3412.0)[h]	(3361.0)[h]	-51.0

[a] $\Delta R_{C–N} = R_{C–N}(Ⅱ) - R_{C–N}(Ⅰ)$; [b] $\Delta R_{N–H} = R_{N–H}(Ⅱ) - R_{N–H}(Ⅰ)$; [c] $\Delta\nu_{as\ N–H} = \nu_{as\ N–H}(Ⅱ) - \nu_{as\ N–H}(Ⅰ)$; [d] $\Delta\nu_{s\ N–H} = \nu_{s\ N–H}(Ⅱ) - \nu_{s\ N–H}(Ⅰ)$; [e] From Ref. 48; [f] From Ref. 49; [g] From Ref. 10; [h] From Ref. 50.