

Electronic Supplementary Information: Comprehensive theoretical study of positron binding and annihilation properties of hydrogen bonded binary molecular clusters

Daisuke Yoshida,^{*,†,‡} Yukiumi Kita,[‡] Tomomi Shimazaki,[‡] and Masanori
Tachikawa

[†]*Nishina Center for Accelerator-Based Science, RIKEN, Hirosawa 2-1, Wako 351-0198,
Japan*

[‡]*Quantum Chemistry Division, Yokohama City University, Seto 22-2, Kanazawa-ku,
Yokohama 236-0027, Japan*

E-mail: daisuke.yoshida.zc@riken.jp

S1. Numerical data for hydrogen bonding clusters

In the main body of our paper, we analyzed the positron affinity PA using various chemical properties such as the magnitude of the dipole moment, the dipole polarizability, and the atomic charge density characteristics for the parent hydrogen bonding clusters $H_nX - H_mY$. Table S1 shows the isotropic total polarizabilities, hydrogen bond distances, and atomic charge differences estimated by the natural population analysis (NPA) for parent hydrogen bonding clusters (without a positron). All other numerical data used for regression analyses are available in the main body of the paper.

Table S1: Hydrogen bond distances R_{HB} , isotropic total polarizabilities α , and atomic charge differences ΔQ_A evaluated by NPA for atoms A of the hydrogen bonded binary molecular clusters $\text{H}_n\text{X} - \text{H}_m\text{Y}$.

H_mY	H_nX	R_{HB} (Å)	α (bohr ³)	Charge differences ΔQ_A (electrons) for atoms A							
				ΔQ_Y	$\Delta Q_{\text{H}_d'}$	ΔQ_{H_d}	ΔQ_X	$\Delta Q_{\text{H}_{\text{ai}}}$	$\Delta Q_{\text{H}_{\text{ao}}}$	ΔQ_{H_a}	$ \Delta Q_{\text{d/a}} $
FH	FH	1.852	9.41	-0.028	0.019	-	-0.007	0.016	-	0.016	0.009
	HCl	2.316	21.23	-0.021	0.009	-	-0.001	0.012	-	0.012	0.011
	H ₂ O	1.708	12.83	-0.057	0.030	-	-0.017	0.000	0.022	0.043	0.026
	H ₂ S	2.286	28.19	-0.037	0.011	-	-0.010	0.000	0.018	0.036	0.026
	NH ₃	1.696	16.92	-0.083	0.028	-	-0.008	0.021	0.021	0.062	0.055
	PH ₃	2.356	33.93	-0.040	0.012	-	-0.023	0.017	0.017	0.051	0.028
HCl	FH	2.063	21.29	-0.032	0.025	-	-0.004	0.011	-	0.011	0.007
	HCl	2.533	33.18	-0.022	0.013	-	0.001	0.008	-	0.008	0.009
	H ₂ O	1.901	25.08	-0.066	0.043	-	-0.009	0.000	0.016	0.031	0.023
	H ₂ S	2.480	40.70	-0.042	0.017	-	-0.003	0.000	0.014	0.028	0.025
	NH ₃	1.810	29.99	-0.114	0.050	-	0.009	0.018	0.018	0.054	0.063
	PH ₃	2.576	46.75	-0.042	0.019	-	-0.014	0.012	0.012	0.037	0.023
H ₂ O	H ₂ O	1.951	16.61	-0.037	0.033	-0.006	-0.016	0.000	0.013	0.025	0.010
	H ₂ S	2.537	32.00	-0.021	0.015	-0.003	-0.019	0.000	0.014	0.028	0.009
	NH ₃	1.696	20.94	-0.049	0.042	-0.011	-0.012	0.012	0.009	0.031	0.019
	PH ₃	2.356	37.94	-0.019	0.016	-0.005	-0.020	0.011	0.008	0.028	0.008
H ₂ S	H ₂ O	2.216	32.17	-0.053	0.046	0.002	-0.010	0.000	0.008	0.016	0.006
	H ₂ S	2.804	47.61	-0.035	0.024	0.004	-0.001	0.000	0.004	0.009	0.008
	NH ₃	1.810	36.82	-0.070	0.058	-0.003	-0.002	0.006	0.006	0.017	0.015
	PH ₃	2.576	53.65	-0.033	0.026	0.002	-0.011	0.006	0.005	0.017	0.005
NH ₃	NH ₃	2.276	25.45	-0.028	0.036	-0.007	-0.006	0.007	0.003	0.012	0.006

In Table S1, α and ΔQ_A are estimated by the natural population analysis (NPA) with the HF wave functions (see the main paper for detailed methods). $\Delta Q_{H'_d}$ and ΔQ_{H_d} mean ΔQ_{AS} for a H atom of the donated proton and a H atom free from the hydrogen bond (a HB-free H atom) of the proton donor unit $H_m Y$, respectively. $\Delta Q_{H_{ai}}$ and $\Delta Q_{H_{ao}}$ mean ΔQ_{AS} for in-plane and out-of-plane H atoms with respect to the mirror plane for the C_s symmetric geometries of the hydrogen bonded binary molecular clusters. ΔQ_{H_a} is the sum over $\Delta \rho_A$ for all H atoms included in a proton acceptor, e.g., $\Delta Q_{H_a} = \Delta Q_{H_{ai}} + 2 \times \Delta Q_{H_{ao}}$ for NH_3 . $|\Delta Q_{H_{d/a}}|$ indicates the magnitude of the total atomic charge differences for both proton donor (d) and acceptor (a), where $\Delta Q_a = -\Delta Q_d > 0$.

S2. Positron structure

Figure S1 shows positron densities for all hydrogen bonded binary molecular clusters and P–P bond bridged $(\text{PH}_3)_2$ cluster, calculated by the CISD method with aug-cc-pVTZ electronic and heavy atom-centered $[7s6p3d2f1g]$ positronic basis sets (see the main paper for calculational details). All of these hydrogen bonded systems have nonzero gross dipole moments indicated by blue arrows, while $(\text{PH}_3)_2$ exhibits zero gross dipole moment but local dipole moments of PH_3 moieties directing opposite to each other. In the former cases, their positron density maxima ρ^p_{max} enclosed by the deep purple color isodensity surface are located around heavy atoms of the proton donor units to align with the dipole moment vectors. The extent of the positron density appears to evade both hydrogen atoms of the donor due to repulsions to less-shielded nuclear charges (protons) by their inorganic polar bonding. In particular systems containing a H atom-rich donor or acceptor, the positron density extends to near a heavy atom of the proton acceptor molecular unit. Such delocalization characteristics can be considered to contribute to the enhancement of the total electron–positron contact density δ_{ep} due to the increase of local electron–positron collision probabilities, demonstrated in Figure 7 in the main paper.

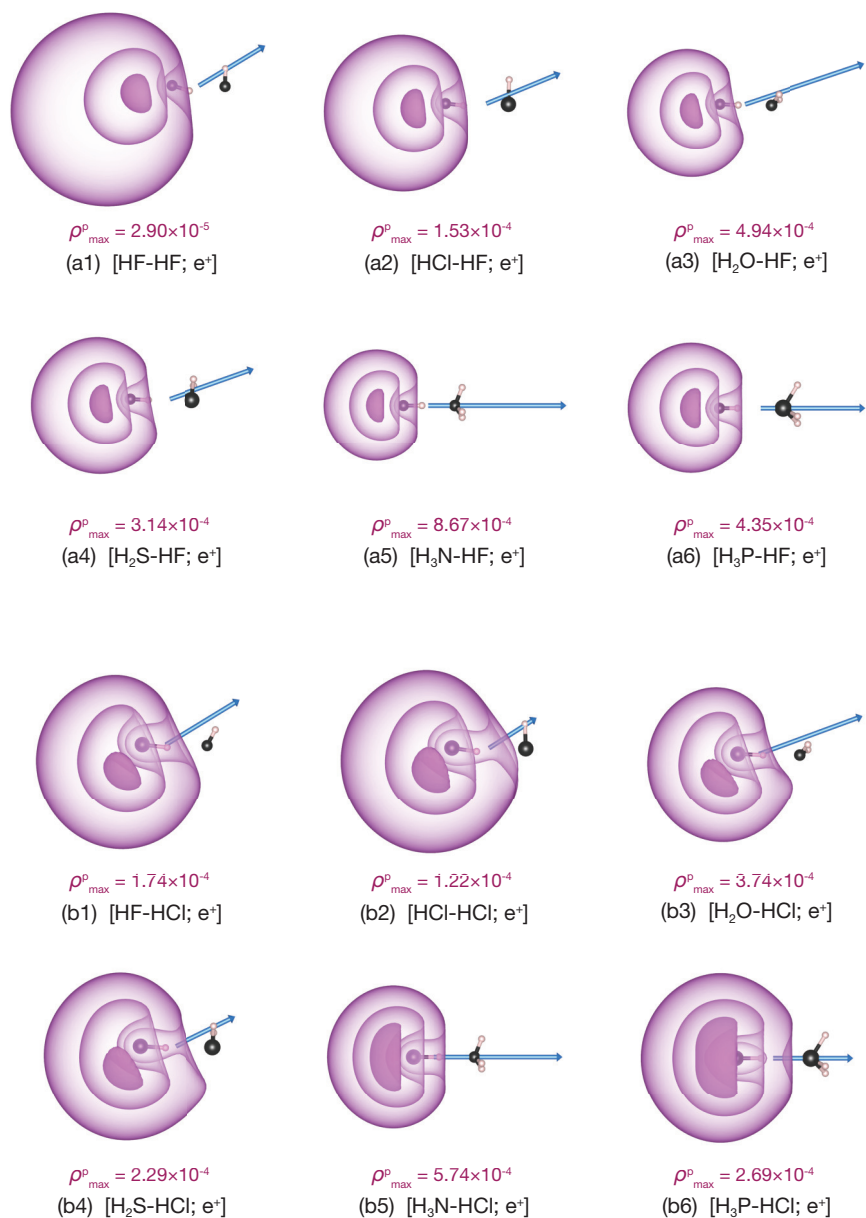


Figure S1: Positron densities for binary molecular clusters. (a), (b), (c), (d) and (e) include hydrogen bonding clusters with proton donors of FH, HCl, H₂O, H₂S, and NH₃, respectively, and only (f) is the PH₃ dimer with van der Waals bonding scheme. Isodensity surfaces with 90, 60, and 30 % of the maximum density ρ_{\max}^p are shown from inner to outer, and the blue arrows are dipole moment vectors directing from negative to positive ends. Heavy and H atoms are shown by the black and white balls, respectively, and the proton donor is placed at the left side in each figure.

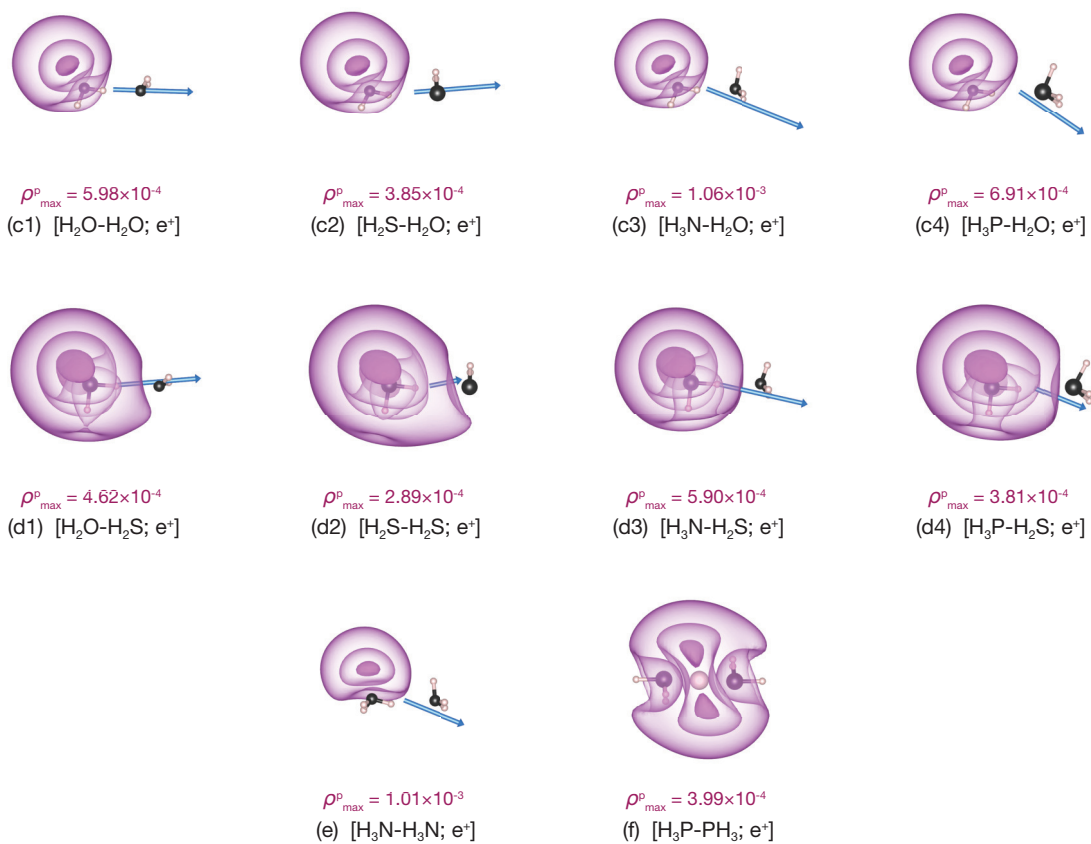


Figure S1: (Continued) Positron densities for binary molecular clusters.

S3. Multiple regression analysis for positron affinity

We have presented the multiple linear regression analyses for PA with the electrostatic properties and charge characteristics in the main paper. We also examined the conventional linear fitting for PA with the magnitude of the dipole moment μ and the total polarizability α found in Table S1. The result of this multiple regression analysis is shown in Figure S2, where symbols are plotted in the same manner with the main paper.

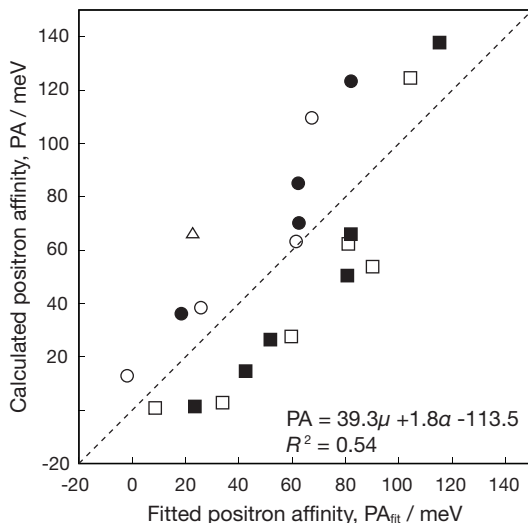


Figure S2: Multiple linear regression for PA (in meV) with the magnitude of the dipole moment, μ (in debye), and the total isotropic polarizability, α (in bohr³). Open and closed squares, open and closed circles, and an open triangle show values for hydrogen bonding clusters with FH, HCl, H₂O, H₂S, and NH₃ donors, respectively.

This fitting somewhat improved agreement by the coefficient of determination $R^2 = 0.54$ in comparison with the single regression with μ , which showed $R^2 = 0.39$. However, this weak linearity of the regression model is still insufficient to valid the effective parameters to reproduce calculated PAs. As shown in Figure S2, obviously, there are still significant variances from the fitting function; clusters with the H atom-rich donors such as H₂Y and H₃Y (Y is a heavy atom of a proton donor) indicated by circles and a triangle are mostly upper bound relative to $PA = PA_{\text{fit}}$, whereas systems with HY type donors indicated by squares tend to be lower bound to $PA = PA_{\text{fit}}$. This data separation tendency implies that the number of hydrogen atoms is likely to be a more effective parameter to describe

dependence on donor substitutions. In addition, regarding the fitting coefficients of the fitted function (embedded in Figure S2), the contribution of α is not so large relative to μ as well as N_{H} shown in the main paper.

Furthermore, we performed the multiple regression analysis to examine effects including the third parameter. Table S2 shows the results of the linear regression analyses with respect to the magnitude of the dipole moment, μ , the number of HB-free H atoms, N_{H} , and an isotropic polarizability term. In both cases of including the polarizability α_{A} for the proton acceptor and including the total polarizability α in the regression formula, these shows the determination coefficients $R^2 = 0.79\text{--}0.83$, which clearly does not improve the reproducibility compared to the $\mu\text{-}N_{\text{H}}$ model showing $R^2 = 0.80$. Inclusion of the polarizability α_{D} for the proton donor can highly improved agreements relative to those above.

Qualities of these multiple regression models can be evaluated by using Akaike information criterion (AIC), which estimate the quality of a fitting model relative to those of other models. In general, when a model gives a AIC value lower than the others, it is considered to be better than other models. As shown in Table S2, both regression models including α_{A} and α do not almost change AIC values compared to the $\mu\text{-}N_{\text{H}}$ model, and only including α_{D} clearly decreases its AIC. Hence, we have concluded that other parameters represented by N_{H} specific to the hydrogen bonding clusters and α_{D} qualified as the local polarizability of the cluster are effective factors to the positron affinity.

Table S2: Linear regression analysis of the positron affinity with respect to the electrostatic properties. The data marked in bold are shown in the main paper.

Descriptors	R^2	AIC
μ, N_{H}	0.80	185
$\mu, N_{\text{H}}, \alpha$	0.83	183
$\mu, N_{\text{H}}, \alpha_{\text{A}}$	0.79	187
$\mu, N_{\text{H}}, \alpha_{\text{D}}$	0.91	168

S4. Electronic charge density analysis

In the main paper we discussed electronic structure changes in terms of electron density differences induced by the hydrogen binding and positron attachment (see the main paper for details of evaluations). Figure S3 shows total density differences, $\Delta\rho^e$, for all calculated systems, where red and blue isosurfaces show the density enhancement and depletion, respectively. As discussed in the main paper, for loosely bound positronic complexes, major parts of these density changes are induced by formations of the hydrogen bonds, while for relatively strongly bound positronic complexes, there are significant density changes by the positron binding, which are competitive to influences from hydrogen bonding. The former part appears like long-range polarization to strengthen polarity of the cluster. Such a density flow behavior is facilitated by the external fields of a bound positron.

The electron density is found to increase in the vicinity of HB-free H atoms especially in (c1) $\text{H}_2\text{O} - \text{H}_2\text{O}$, (c3) $\text{H}_3\text{N} - \text{H}_2\text{O}$, and (e) $\text{H}_3\text{N} - \text{H}_3\text{N}$. These atomic charge differences consistently exhibit $\Delta Q_{\text{H}_{i'}} < 0$ (i.e., the increase of the negative charge). In contrast, clusters with the H_2S proton donor clearly show electron density depletions in the vicinity of HB-free H atoms, which also mostly exhibit $\Delta Q_{\text{H}_{i'}} > 0$.

In order to quantify a correlation between the positron affinity and electron density difference shown in Figure S3, we performed the linear regression analysis of the positron affinity PA employing changes in the atomic charges calculated via the NPA analysis presented in Table S1. Table S3 shows results of the linear regression analysis with respect to ΔQ_{AS} . As we explain in the main paper, the degree of negativity of the heavy atom (Y) of the proton donor, represented by ΔQ_Y , has a dominant influence on PA. Including an additional effective parameter, we found that the atomic charge differences only for H atoms of the proton donor can be effective, whereas those for H atoms of the proton acceptor do not improve the quality of the fitting model compared to the single regression model.

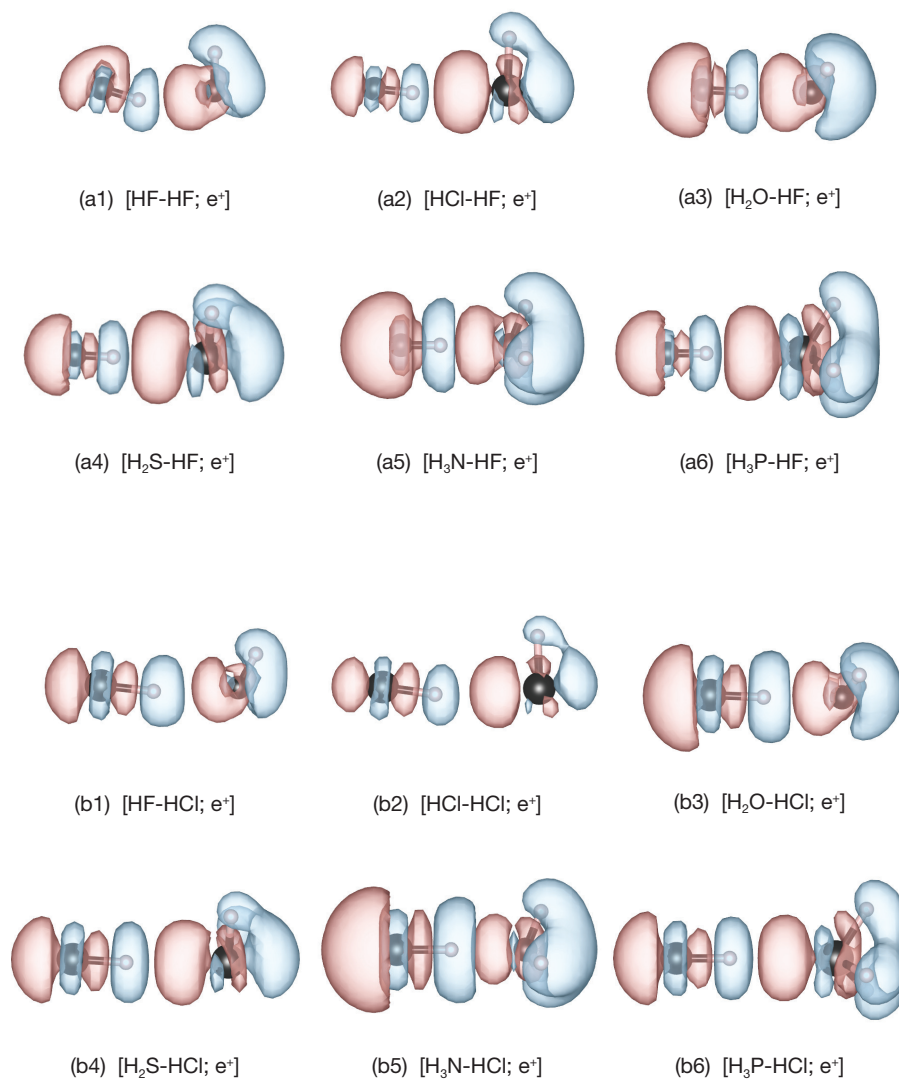


Figure S3: Electron density difference induced by the formation of the hydrogen bond and the positron binding. Red and blue isosurfaces show the electron density enhancement ($\Delta\rho^e > 0$) and depletion ($\Delta\rho^e < 0$) with the magnitude of 0.05 a.u..

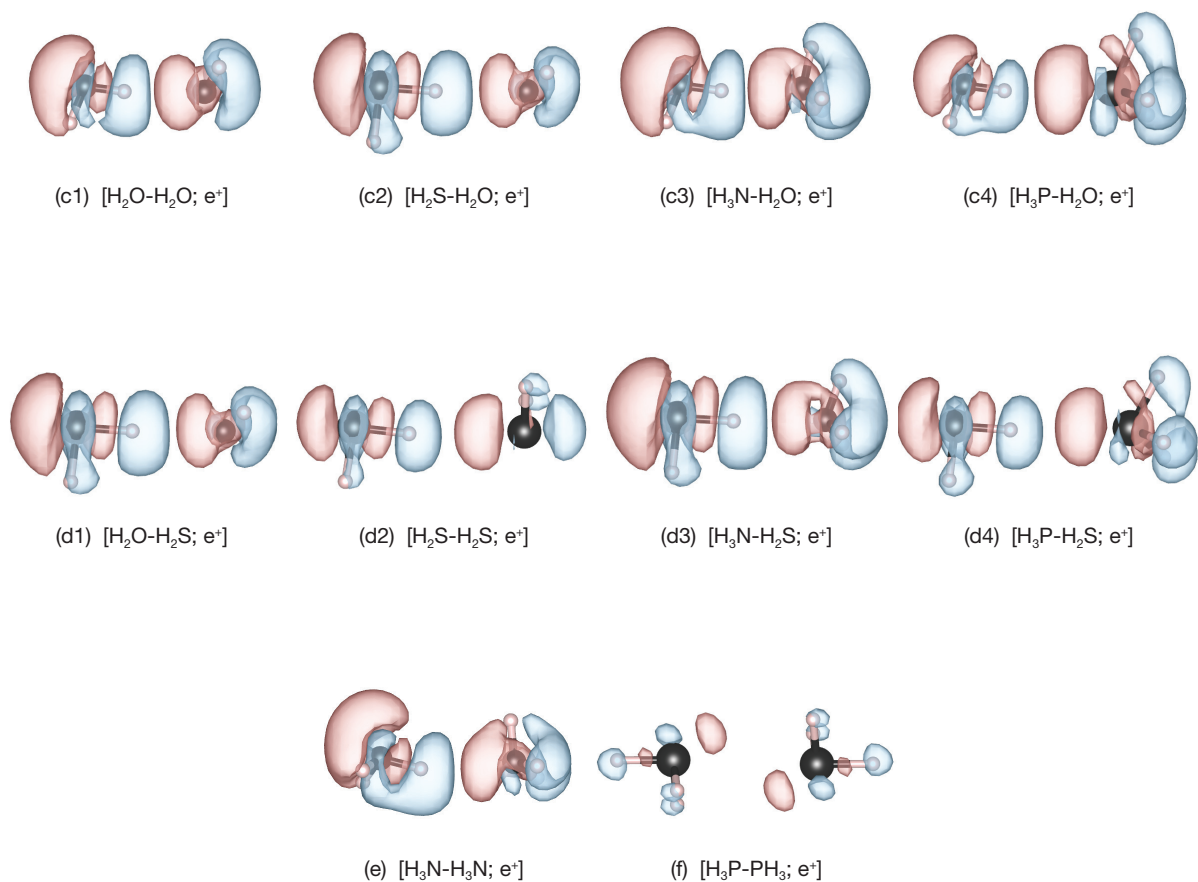


Figure S3: (Continued) Electron density difference induced by the formation of the hydrogen bond and the positron binding.

Table S3: Linear regression analysis of the positron affinity with respect to atomic charge differences. In this analysis, atomic charge density differences ΔQ_A shown in Table S1 are used as descriptors. The data marked in bold are shown in the main paper.

Descriptors	R^2
ΔQ_Y	0.65
$\Delta Q_Y, \Delta Q_{H_{d'}}$	0.71
$\Delta Q_Y, \Delta Q_{H_d}$	0.73
$\Delta Q_Y, \Delta Q_{H_{ai}}$	0.64
$\Delta Q_Y, \Delta Q_{H_{ao}}$	0.61
$\Delta Q_Y, \Delta Q_X$	0.66

S5. Characterization of hydrogen bonding clusters

In the main paper, we presented the effective regression model with μ , N_{H} , and α_{D} , alternative to the conventional (μ and α) model, and discussed roles of these additional effective parameters on the basis of the atomic charge analysis. As extended data supplementations, we also considered roles of other parameters excluded from fitting PA, such as, for example, the local polarizability of the proton acceptor unit as well as geometrical properties.

Figure S4 shows the linear regression analyses for the magnitude of the dipole moment, μ , of the parent cluster (without a positron) using the hydrogen bond length R_{HB} and the molecular polarizability α_{A} of the proton acceptor for hydrogen binding clusters. The least-squares fitting only with R_{HB} (a) shows a sufficient linearity with the coefficient of determination $R^2 = 0.67$. It is clear that there is a negative correlation between μ increased by forming the hydrogen bond and R_{HB} . As shown in (b) including α_{A} as the second descriptor improved agreement to $R^2 = 0.77$, where α_{A} has a positive correlation with μ . Thus, we have found that α_{A} may have a role to facilitate the dipole-dipole interaction to form the hydrogen bond, with the response induced by the dipole field of the donor molecule, which results in the increase of the gross dipole moment of the cluster.

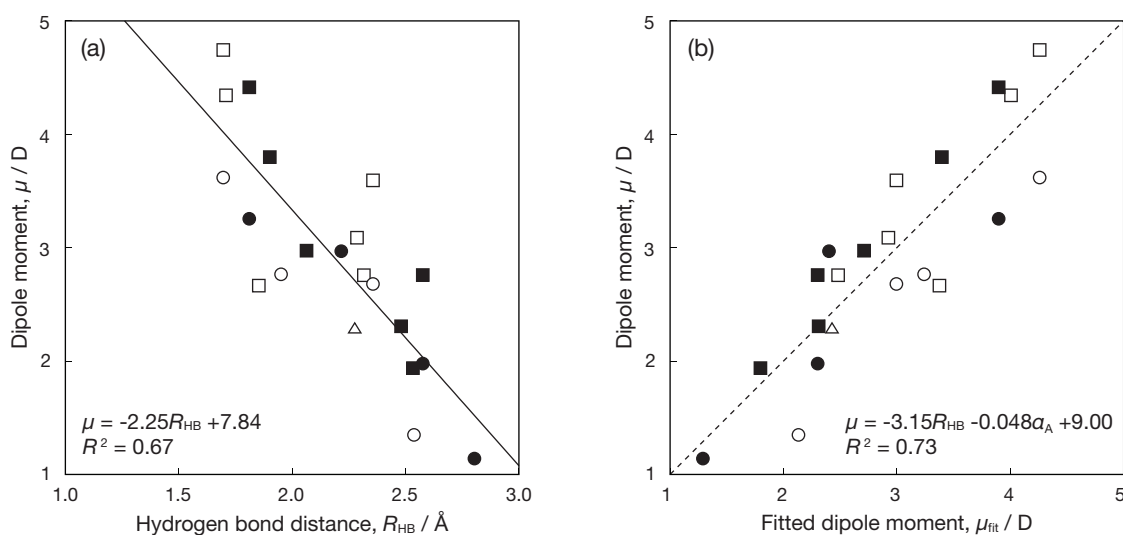


Figure S4: Linear regression analysis for μ (in debye) with the hydrogen bond distance R_{HB} (in \AA) and the isotropic polarizability α_A of the proton-donor molecule (in bohr^3); (a) μ with R_{HB} and (b) μ with the fitted function $\mu_{\text{fit}}(R_{\text{HB}}, \alpha_A)$. A solid line embedded in (a) shows the fitted linear function, and a dashed line in (b) indicates $\mu = \mu_{\text{fit}}$. Open and closed squares, open and closed circles, and an open triangle show values for hydrogen bonding clusters with FH, HCl, H_2O , H_2S , and NH_3 donors, respectively.