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Supporting information for article:

Quantitative analysis of intermolecular interactions in orthorhombic rubrene

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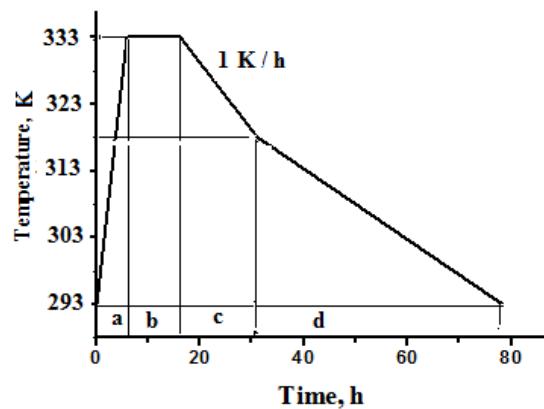


Figure S1 The temperature profile for the crystal growth of rubrene: (a) the rubrene solution temperature was raised to 333K (b) the temperature was maintained at 333K for 10h (c) the solution was cooled to the saturation point (318K) at a rate of 1K/h (d) the solution is cooled to room temperature at a rate of $\leq 0.5\text{K/h}$ during which the crystals form.

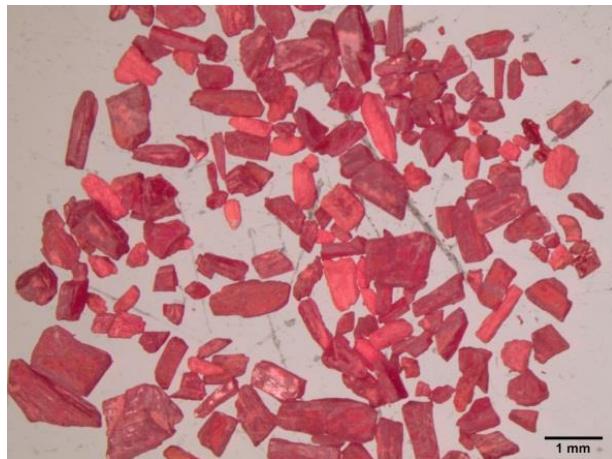


Figure S2 Optical micrograph showing the obtained single crystals of rubrene.

Table S1 Crystallographic and refinement details of 20 K synchrotron data collected at the BL02B1 beamline at SPring-8, Japan.

Radiation Source	Synchrotron
Empirical Formula	C ₄₂ H ₂₈
Formula Weight, g mol ⁻¹	532.64
Crystal size (μm)	100
Crystal system	Orthorhombic
Space Group	Cmca
λ, Å	0.35312
a, Å	26.7965(5)
b, Å	7.1599(1)
c, Å	14.1519(3)
V, Å ³	2715.19(9)
Z	4
F(000)	1120
T, K	20
ρ, g cm ⁻³	1.299
μ, mm ⁻¹	0.007
T _{max} , T _{min}	1.0000, 0.9993
sin(θ)/λ _{max} , Å ⁻¹	1.51
N _{meas} , N _{uniq}	441669, 19909
Redundancy	22.2
Completeness	1.000
R _{int}	0.0514
N _{obs} , N _{var} , (3σ)	14111, 384
R(F ²), wR(F ²) (I>2σ(I))	0.0192, 0.0392
Goodness of fit	1.043
Δρ _{min/max} eÅ ⁻³ all data, sinθ/λ<1.1Å ⁻¹	-0.188/0.226, -0.089/0.133

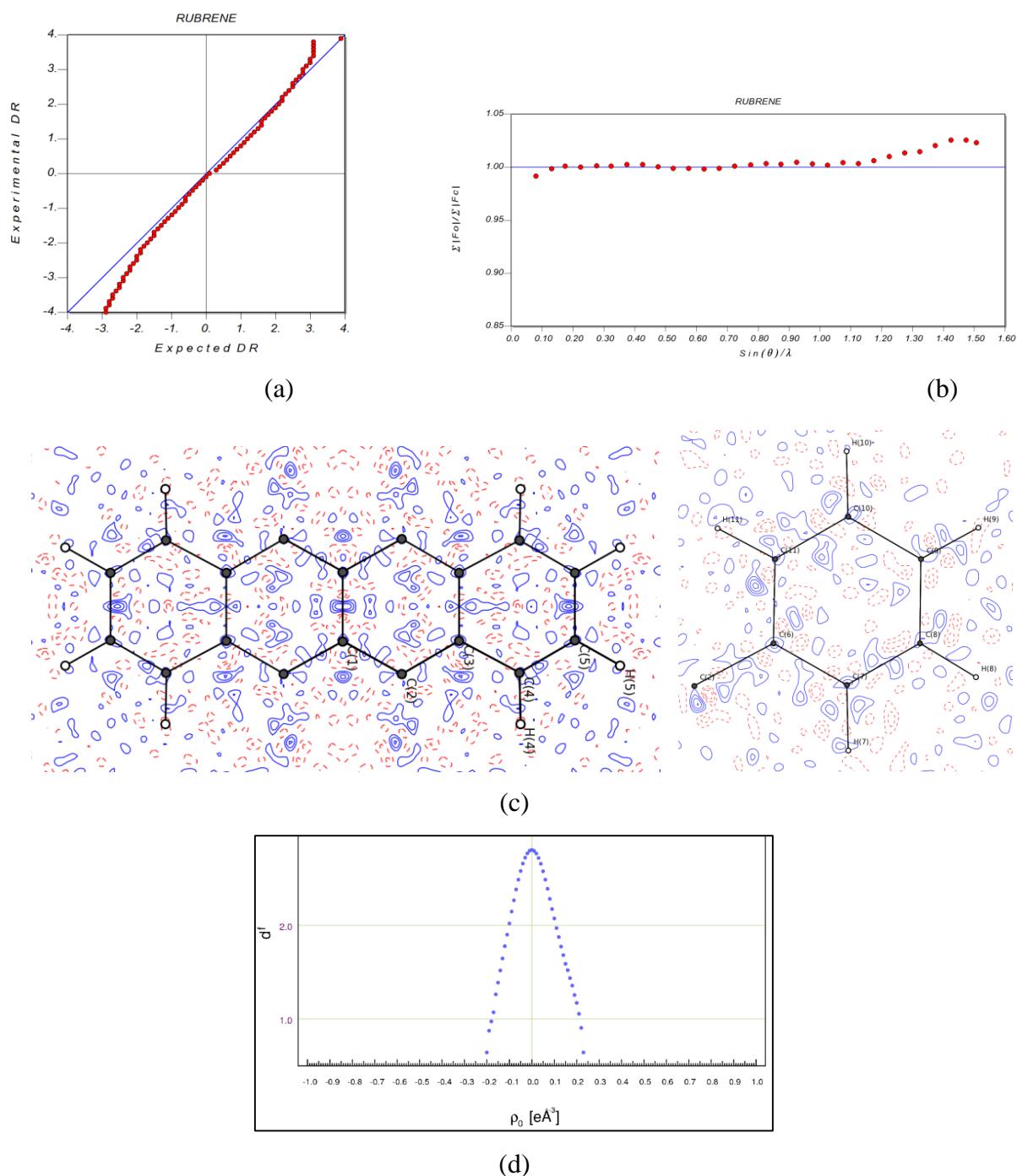


Figure S3 The quality of the ED model at 20 K was estimated by (a) the normal probability plot (b) a variation of scale factor with resolution (c) residual density maps are at ± 0.05 contour intervals and (d) the fractal dimension plot. These all suggest that an excellent data quality and a good fit of the multipole model of electron density.

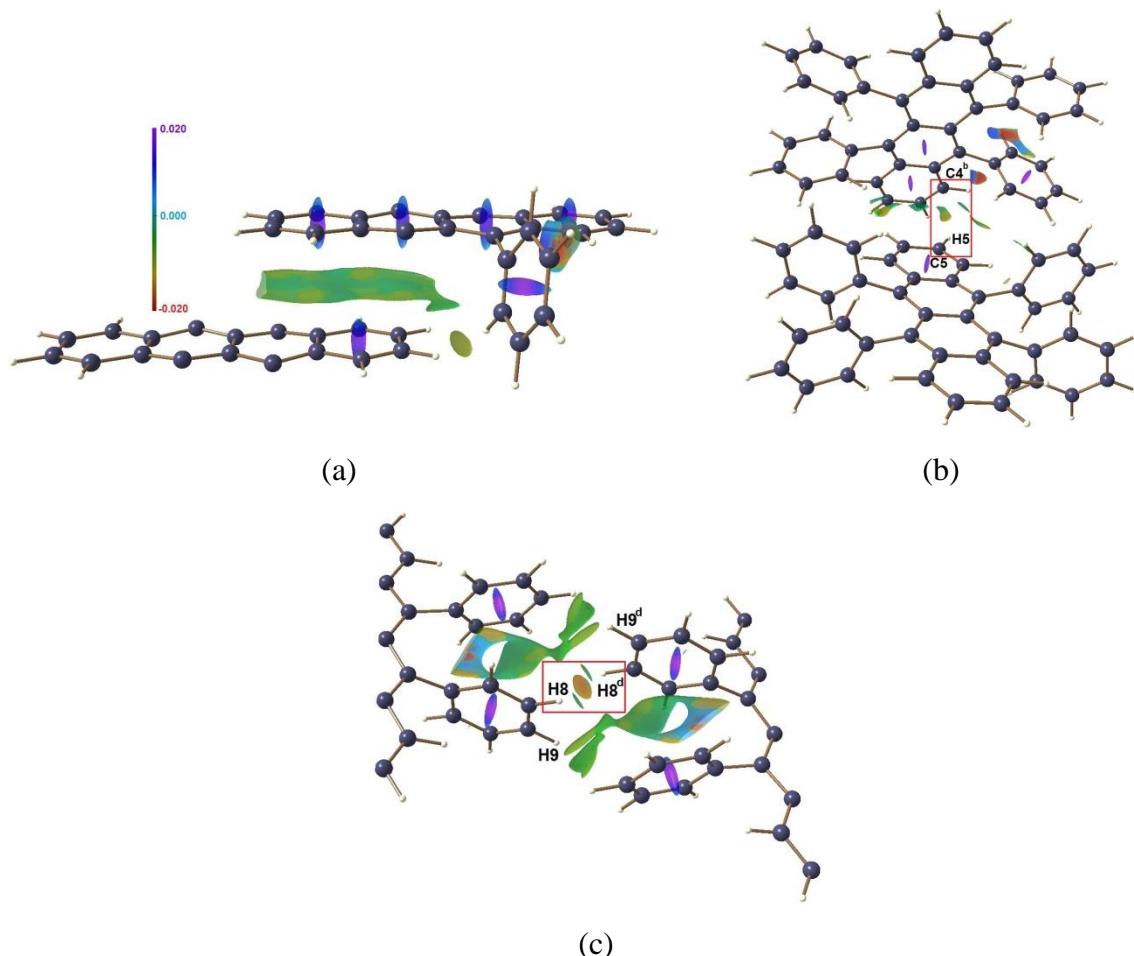


Figure S4 RDG-based NCI isosurfaces obtained from the experimental ED model at 20 K for (a) $C_{\pi}\cdots C_{\pi}$ stacking interactions (b) $C4\cdots H5$ interaction and (c) homopolar $H8\cdots H8$ bonds. NCI surfaces correspond to $RDG = 0.6$ au. The surfaces are colored on a red-green-blue scale ($-0.020 < \text{sign}(\lambda_2)\rho < 0.034$ au). Red, green and blue indicate strong **stabilizing**, intermediate and **destabilizing** overlap regions, respectively.

Table S2 List of intra-molecular BCP's obtained from the experimental and theoretical ED models at 100 K and 20 K. The values reported in first, second and third lines correspond to the experimental multipole model, theoretical multipole model and theory from PROAIM, respectively.

Temperature	Bond	R _{ij} (Å)	ρ _b (eÅ ⁻³)	∇ ² ρ _b (eÅ ⁻⁵)	ε
100 K	C1-C2	1.4264	2.022	-18.573	0.26
			1.960	-15.190	0.20
			1.960	-18.200	0.20
	C2-C3	1.4065	2.133	-21.053	0.18
			2.035	-16.543	0.19
			2.040	-19.600	0.23
	C3-C4	1.4373	2.011	-19.129	0.14
			1.922	-15.145	0.14
			1.931	-18.200	0.14
	C4-C5	1.3658	2.290	-25.029	0.17
			2.191	-19.333	0.23
			2.192	-22.600	0.26
	C4-H4	1.0839	1.906	-24.763	0.06
			1.918	-20.889	0.03
			1.918	-23.600	0.02
	C5-H5	1.0876	1.899	-22.485	0.06
			1.889	-20.810	0.03
			1.886	-23.000	0.02
	C2-C6	1.4972	1.870	-17.167	0.01
			1.737	-11.918	0.03
			1.737	-15.000	0.03
	C6-C7	1.3979	2.156	-21.207	0.13
			2.084	-17.367	0.18

			2.065	-20.200	0.21
C7-C8	1.3920	2.239	-24.182	0.17	
		2.112	-17.966	0.20	
		2.092	-20.900	0.21	
C8-C9	1.3942	2.160	-23.294	0.26	
		2.096	-17.473	0.19	
		2.086	-20.900	0.20	
C9-C10	1.3956	2.201	-24.165	0.14	
		2.084	-17.226	0.18	
		2.073	-20.500	0.20	
C10-C11	1.3965	2.210	-22.658	0.16	
		2.088	-17.405	0.19	
		2.071	-20.500	0.21	
C11-C6	1.3982	2.121	-21.371	0.20	
		2.087	-17.401	0.20	
		2.067	-20.200	0.22	
C7-H7	1.0869	1.928	-23.980	0.05	
		1.901	-20.441	0.03	
		1.896	-23.200	0.02	
C8-H8	1.0856	1.753	-18.682	0.05	
		1.896	-20.076	0.02	
		1.894	-23.200	0.02	
C9-H9	1.0860	1.714	-20.759	0.02	
		1.897	-20.321	0.02	
		1.891	-23.100	0.02	
C10-H10	1.0882	1.860	-20.918	0.06	
		1.899	-20.496	0.02	
		1.889	-23.100	0.02	

	C11-H11	1.0839	1.926	-23.574	0.05
			1.917	-20.900	0.03
			1.903	-23.400	0.02
20 K	C1-C2	1.4274	1.982	-18.499	0.21
			1.945	-14.782	0.21
			1.960	-18.160	0.20
	C2-C3	1.4068	2.088	-20.380	0.23
			2.028	-16.395	0.20
			2.039	-19.613	0.22
	C3-C4	1.4391	1.972	-18.349	0.17
			1.909	-14.842	0.15
			1.924	18.018	0.14
	C4-C5	1.3666	2.243	-23.613	0.26
			2.179	-18.977	0.24
			2.189	-22.515	0.26
	C4-H4	1.0839	1.857	-20.836	0.06
			1.913	-20.757	0.03
			1.917	-23.639	0.02
	C5-H5	1.0876	1.867	-21.924	0.06
			1.884	-20.680	0.03
			1.886	-23.037	0.02
	C2-C6	1.4979	1.705	-13.428	0.06
			1.729	-11.782	0.04
			1.735	-14.997	0.03
	C6-C7	1.4001	2.111	-20.808	0.28
			2.066	-16.956	0.18
			2.056	-20.046	0.21
	C7-C8	1.3941	2.074	-19.849	0.17
			2.095	-17.530	0.19

			2.084	-20.718	0.20
C8-C9	1.3975	2.126	-20.683	0.16	
		2.071	-16.930	0.19	
		2.070	-20.509	0.20	
C9-C10	1.3965	2.128	-21.019	0.27	
		2.070	-16.957	0.20	
		2.069	-20.448	0.20	
C10-C11	1.3975	2.072	-20.369	0.22	
		2.072	-17.014	0.19	
		2.065	-20.336	0.21	
C11-C6	1.4005	2.106	-19.909	0.17	
		2.069	-16.984	0.20	
		2.057	-20.013	0.22	
C7-H7	1.0868	1.892	-21.802	0.04	
		1.895	-20.337	0.03	
		1.896	-23.211	0.02	
C8-H8	1.0855	1.874	-21.377	0.07	
		1.894	-20.089	0.02	
		1.894	-23.208	0.02	
C9-H9	1.0862	1.855	-21.617	0.04	
		1.892	-20.262	0.02	
		1.891	-23.133	0.02	
C10-H10	1.0865	1.864	-21.313	0.05	
		1.894	-20.405	0.02	
		1.889	-23.099	0.02	
C11-H11	1.0850	1.832	-21.273	0.09	
		1.913	-20.828	0.03	
		1.903	-23.386	0.02	

Table S3 Integrated net atomic charges $q(\Omega)$ derived from the QTAIM analysis

Atom	100 K					20 K			
	Experiment	theory, multipole	theory, LCGTF	theory, Gaussian		experiment	theory, multipole	theory, LCGTF	theory, Gaussian
C1	-0.07	-0.03	0.00	-0.01	-0.05	-0.03	0.00	-0.01	
C2	0.04	-0.02	0.01	-0.02	-0.02	-0.02	0.01	-0.02	
C3	-0.01	-0.02	0.00	-0.01	-0.03	-0.02	0.00	-0.01	
C4	-0.02	-0.08	0.02	-0.02	-0.03	-0.03	0.02	-0.02	
C5	-0.02	-0.04	0.00	-0.02	-0.04	-0.02	0.00	-0.02	
C6	-0.03	-0.02	-0.01	0.00	-0.03	-0.02	-0.01	0.00	
C7	-0.07	-0.03	0.00	-0.01	-0.04	-0.02	0.00	-0.01	
C8	-0.03	-0.04	0.01	-0.01	-0.02	-0.02	0.01	-0.01	
C9	-0.04	-0.03	0.01	-0.01	-0.04	-0.02	0.01	-0.01	
C10	-0.08	-0.01	0.01	-0.02	-0.03	-0.02	0.01	-0.01	
C11	0.09	-0.03	0.01	-0.01	-0.02	-0.02	0.01	-0.01	
H4	0.01	0.03	-0.01	0.04	0.05	0.03	-0.01	0.04	
H5	-0.05	0.04	-0.01	0.02	0.04	0.04	-0.02	0.02	
H7	0.05	0.04	-0.01	0.02	0.06	0.03	-0.01	0.02	
H8	0.06	0.09	-0.01	0.01	0.04	0.03	-0.01	0.01	
H9	0.09	0.08	0.00	0.02	0.05	0.03	0.00	0.02	
H10	0.03	0.04	-0.02	0.02	0.05	0.04	-0.02	0.02	
H11	0.05	0.03	-0.01	0.02	0.06	0.04	-0.01	0.02	

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Table S4 Lattice energy and intermolecular interaction energies of selected molecular dimers (kJmol^{-1}) in rubrene obtained from the PIXEL calculations using the ED from the MP2 method. The values reported in first and second lines correspond to the crystal geometry at 100 K and 20 K, respectively. Symmetry operations are listed in Table 1.

molecular dimers	Interaction Distance (\AA)	Centroid- centroid distance (\AA)	E_{es}	E_{pol}	E_{disp}	E_{rep}	E_{tot}
Lattice energy	-	-	-55.9	-34.8	-305.0	171.8	-223.9
	-	-	-57.4	-35.9	-309.7	178.2	-224.9
$\text{C}_{\pi}\cdots\text{C}_{\pi}$ stacking ^a (dimer I)	3.706(1)	7.160(2)	-8.1	-14.2	-110.5	64.0	-68.7
	3.694(1)	7.160(2)	-8.3	-14.4	-112.1	66.2	-68.6
$\text{C4}\cdots\text{H5}^{\text{b}}$ (dimer II)	2.825(1)	7.953(3)	-15.8	-6.7	-62.1	36.5	-48.0
	2.817(1)	7.930(2)	-16.2	-7.0	-63.1	37.7	-48.5
$\text{H8}\cdots\text{H8}^{\text{d}}$ (dimer III)	2.268(1)	13.875(4)	-7.0	-2.8	-24.2	15.2	-18.8
	2.264(1)	13.868(3)	-7.1	-2.9	-24.5	15.7	-18.8
$\text{H9}\cdots\text{H9}^{\text{e}}$ (dimer IV)	2.667(1)	15.170(2)	-1.1	-0.4	-7.6	2.5	-5.5
	2.623(1)	15.152(2)	-1.2	-0.4	-7.8	2.7	-5.6

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