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Visualizing Noncovalent Interactions and Property Prediction of Submicron-Sized Charge-Transfer Crystals from \textit{ab-initio} Determined Structures

Zhong-Peng Lv,* Divya Srivastava, Kevin Conley, Tero-Petri Ruoko, Hongyi Xu, Molly Lightowler, Xiaodan Hong, Xiaqi Cui, Zhehao Huang, Taimin Yang,* Hai-Ying Wang,* Antti J. Karttunen, and Lennart Bergström

The charge-transfer (CT) interactions between organic compounds are reflected in the (opto)electronic properties. Determining and visualizing crystal structures of CT complexes are essential for the design of functional materials with desirable properties. Complexes of pyranine (PYR), methyl viologen (MV), and their derivatives are the most studied water-based CT complexes. Nevertheless, very few crystal structures of CT complexes have been reported so far. In this study, the structures of two PYRs-MVs CT crystals and a map of the noncovalent interactions using 3D electron diffraction (3DED) are reported. Physical properties, e.g., band structure, conductivity, and electronic spectra of the CT complexes and their crystals are investigated and compared with a range of methods, including solid and liquid state spectroscopies and highly accurate quantum chemical calculations based on density functional theory (DFT). The combination of 3DED, spectroscopy, and DFT calculation can provide important insight into the structure-property relationship of crystalline CT materials, especially for submicrometer-sized crystals.

1. Introduction

In the past few decades, interactions between the electron-rich (donors, D) and electron-deficient (acceptors, A) molecules have gained considerable attention in organic electronics. This focus on D–A association has led to the exploration of charge-transfer complexes (CTCs).\cite{1,2} The charge-transfer (CT) states at the D–A interface exhibit unique electronic and optoelectronic properties that hold great promise for organic electronics, such as organic field-effect transistors,\cite{3,4} ferroelectrics,\cite{5} organic photovoltaic cells,\cite{6} and organic light-emitting devices.\cite{7-9} To enable the rational design and controlled synthesis of CTCs, substantial efforts have been directed toward understanding the nature of CT states,\cite{10-12} which is heavily influenced by the molecular structures and the noncovalent interactions between D and A molecules.\cite{13} Thus, obtaining the crystal structure of the CTCs became significant for their application. Most well-studied CTC crystals are assembled in low-polarity organic solvents.\cite{14,15} For water-soluble CTCs, though many low-dimension nano assemblies have been reported,\cite{16} well-defined crystals are still sparse, because the complex noncovalent interactions in water always result in
submicron crystals which are too small for X-ray crystallography. Consequently, there are very few reported water-soluble CTC crystal structures, and their structure-property relationship is not well investigated.

Due to the stronger scattering ability of electrons than X-ray photons, 3D electron diffraction (3DED) can determine structures from submicron or nano-sized crystals, such as zeolites, metal-organic frameworks (MOFs), small organic molecules, and proteins. The high-resolution 3DED datasets can provide essential information on structural details, such as hydrogen atoms positions, charge, and molecular chirality.

In this study, we use 3DED to obtain the high-accuracy structures of two submicron-sized CTCs crystals of pyranine (PYRs) and methyl viologen (MVs) derivatives (Scheme 1a,b). To the best of our knowledge, this is the first time that the crystal structures of aqueous CTCs were determined by 3DED. With the high-precision structures, we employed computational methods, e.g., density functional theory (DFT) and time-dependent DFT (TD-DFT) to predict a range of physical properties such as electronic band structures, conductivities, CT mechanism, and optical excitations (Scheme 1c). In addition, we visualized different types of noncovalent interactions, including hydrogen bonding, electrostatic interaction, \( \pi-\pi \) interactions, van der Waals (VDW) interactions, and CT interactions. The CT interactions and the packing geometries of the CTCs were also investigated using Ultraviolet-visible (UV–vis) spectroscopy, photoluminescence (PL) spectroscopy, and nuclear magnetic resonance (NMR). Additionally, we studied the interaction between the PYRs/MVs with another widely used CT molecule as a control (2-anthryltrimethylammonium, ANT).

With our combined experimental and theoretical investigation workflow, we have successfully visualized and comprehensively analyzed the CTCs of PYRs and MVs in both crystalline and aqueous phases.

2. Results and Discussion

2.1. Crystal Structures of PYR-MV Complexes

In \( \text{PYR}_2\text{MVs} \) with a chemical formula of \( \text{Na}([\text{C}_{15}\text{N}_2\text{H}_{16}])\text{C}_{19}\text{O}_{10}\text{S}_3\text{H}_9) \), two sulfonate anions of \( \text{PYR}_2\text{Na}^+ \) link with two crystallographic independent \( \text{Na}^+ \) ions to yield a 1D chain through strong O–Na bonds along the crystallographic b-axis, which was further connected into a 2D network via b-planes (Figure 1a; Table S1, Supporting Information). We have calculated the distances and/or angles of \( \pi-\pi \) interactions and...
A chemical formula of (C₁₂N₂H₁₄)₁.₅(C₁₆O₁₀S₃H₇) contains one and a half MV₂⁺ guest ions. (b) The 3D framework of PYRₐ-MVₐ is stacked by the 2D networks via nonclassical hydrogen bonds.

Supporting Information). The interaction areas are also closer to the molecule centers, due to the higher symmetry. As shown in Figure 2e, H atoms are enveloped by the electrostatic potential, confirming the existence of H atoms from experimental data.

2.2. Electronic Structures of PYR-MV Complexes

From the crystal structure, we calculated the electronic structures of the two CTCs (Figure 3a,b). The two materials have similar electronic structures as indicated by the atom-projected density of states (PDOS). The states form a continuous band below −1 eV and have a series of intense peaks between −0.1 and 4 eV. The closer π⋯π packing in PYRₐ-MVₐ implies a stronger CT interaction than in PYRₐ-MVₐ. We speculate that the closer packing in PYRₐ-MVₐ is the major reason for their structural difference, where there is not enough space to form a 1D sulfonate sodium chain. Instead of Na⁺, an extra half MV₂⁺ for charge balancing lies between the 1D chains without participating in the CT interaction.

Figure 1. Crystal structure of PYRₐ-MVₐ complex. a) The coordination environments of Na₁ and Na₂, and the 2D network of NaPYR₂⁺ filled with MV₂⁺ guest ions. b) The 3D framework of PYRₐ-MVₐ is stacked by the 2D networks via nonclassical hydrogen bonds.

d) Hirshfeld surface for the donor (left, −0.85 < dₜₙₜ < 1.53) and acceptor (right, −0.45 < dₜₙₜ < 1.69). Red, white, or blue surface color represents shorter, equal, or longer contact distance compared to the sum of the VDW radii, respectively.

e) The electrostatic potential map from experimental data (isosurface value: 0.2 V).

Supporting Information).

The darker red regions indicate the presence of the C–H⋯O hydrogen bonds and lighter ones are weaker short contacts. The π⋯π interaction between the donor and acceptor can be visualized by the triangular-shaped regions (highlighted by white dash circles) on the HS plotted over the shape index (Figure S1, Supporting Information). The π⋯π interaction areas deviated from the center of both donor and acceptor molecules, which is consistent with the off-center stacking geometry of D–A pair in Figure 1c. In the electrostatic potential map (Figure 1e), the electrostatic potential enveloped both the disordered Na⁺ ions and all hydrogen atoms, which further proved the high accuracy of the refined structure.

Different from PYRₐ-MVₐ, the unit cell of PYRₐ-MVₐ with a chemical formula of (C₁₂N₂H₁₄)₁.₅(C₁₆O₁₀S₃H₇) contains one and a half MV₂⁺ and one PYRₐ³⁻, and no host network is formed due to the lack of bridging Na⁺ ions.[34] In Figure 2a, a similar 1:1 D–A–D–A 1D CT chain was formed between the neighboring PYRₐ³⁻ and MV₂⁺ (π⋯π contacts, 3.50 and 3.76 Å). The close proximity of PYRₐ³⁻ and MV₂⁺ implies a stronger CT interaction than in PYRₐ-MVₐ. We speculate that the closer packing in PYRₐ-MVₐ is the major reason for their structural difference, where there is not enough space to form a 1D sulfonate sodium chain. Instead of Na⁺, an extra half MV₂⁺ for charge balancing lies between the 1D chains without participating in the CT interaction. A similar structure was reported in the perylene-TCNQ crystals.[39] A 3D network is further formed via hydrogen bonds between sulfonate anion and hydroxy group (H⋯O, 2.11 Å) and nonclassical hydrogen bonds (H⋯O, 2.36 and 2.38 Å) between MV₂⁺ and sulfonate anion (Figure 2b). From Figure 2c, we found the D–A pair in PYRₐ-MVₐ is more symmetrical and well aligned via the molecular center, compared to PYRₐ-MVₐ. In Figure 2d, both C–H⋯O and O–H⋯O hydrogen bonds are presented as red areas in the HS plot. The shape index plot shows π⋯π interaction areas in PYRₐ-MVₐ are located more loosely (Figure S2, Supporting Information), compared with that in PYRₐ-MVₐ (Figure S1, Supporting Information). The interaction areas are also closer to the molecule centers, due to the higher symmetry. As shown in Figure 2e, H atoms are enveloped by the electrostatic potential, confirming the existence of H atoms from experimental data.
states from C atoms are mixed throughout the energy range. The intense peak just below the Fermi level has contributions from O states and the sharp, unoccupied ones between 2.5 and 4 eV have contributions from H and N states. Thus, the charge is expected to transfer from the PYR electron donor to the MV electron acceptor. This is also illustrated by the charge density of the topmost occupied and bottom unoccupied bands in PYRb-MVb (Figure 3c,d). As expected, the charge density is located on the electron donor molecule in the topmost band and on the electron acceptor molecule in the bottom band. We also confirm that the extra half MVb\(^{2+}\) in PYRs-MVb does not contribute to the CT interaction (Figure S3, Supporting Information).

The crystal conductivities along a, b, and c axes are obtained from the band structures (Figure S4, Supporting Information). Particularly, both crystals are more conductive along the D–A \(\pi\) stacking direction, i.e., b-axis for PYRb-MVb and a-axis for PYRb-MVb. The experimental conductivities \(\sigma\) of the two CTCs are measured from drop-casting thin films on a four-probe setup. The drop-cast thin films of the two complexes have the same structures as their crystals, which is confirmed by comparing the thin film X-ray diffraction patterns with the simulated XRD pattern from the crystallography structure (Figure S5, Supporting Information). The average isotropic conductivity of PYRb-MVb is 3.5 ± 1.7 \(\times\) \(10^{-4}\) S m\(^{-1}\) from six individual samples with a thickness of 300–500 nm (Figure S6, Supporting Information). The conductivity of PYRb-MVb is much lower \(\sigma < 4 \times 10^{-7}\) S m\(^{-1}\). The conductivity difference in the two complexes indicates the structure of the crystal and the donor can largely tune the conductivity of CTCs.\(^{39,40}\) We then compare the experimental conductivity with the calculated isotropic conductivity (Figure 3e,f), which is the mean conductivity in different directions. Assuming both CTCs are p-type doping as typical in organic crystals,\(^{41}\) we speculate the band transport is the major transport mechanism and the conduction is occurring at \(E - E_0 < -0.6\) eV, where the calculated conductivities of PYRb-MVb is higher than that of PYRb-MVb, consistent with the measured values. Both crystals are indirect gap materials as seen in the electronic band structure (Figure S7, Supporting Information). The band dispersion near the Fermi level is weak and likely limits the electrical conductivity via band transport. However, there are direct transitions at slightly higher energy. The lowest energy transition is 2.59 eV from \(\Gamma\) to D in PYRb-MVb and 2.58 eV from \(\Gamma\) to U in PYRb-MVb. The direct bandgap is at the \(\Gamma\)-point and is 2.62 eV and 2.73 eV for PYRb-MVb and PYRb-MVb, respectively.

Figure 2. Crystal structure of PYRb-MVb complex. a) The 2D network is formed by 1D D–A–D–A 1D CT chains via classical and nonclassical hydrogen bonds. b) The 3D framework of PYRb-MVb is stacked by the 2D networks via nonclassical hydrogen bonds. c) A projection of the 1:1 D–A pair from a-axis. The hydrogen atoms are omitted for clarity. d) Hirshfeld surface for the donor molecule (left, \(-1.21 < d_{norm} < 1.61\)) and acceptor (right, \(-0.806 < d_{norm} < 1.932\)). Red, white, or blue surface color represents shorter, equal, or longer contact distance compared to the sum of the VDW radii, respectively. e) The electrostatic potential map from experimental data (isosurface value: 0.2 V).

2.3. UV–Vis and PL Study of PYR-MV Complexes

Spectroscopy characterizations, i.e., UV–vis and PL are employed to further investigate the CT interactions in both solid-state and aqueous phases. We have acquired the solid-state UV–vis and PL spectra from thin film samples drop-cast from the solutions of PYRs, MVs, or their 1:1 mixture. From UV–vis spectra (Figure 4a,b), we can clearly observe a CT band at ca. 460–480 nm in both PYRb-MVb and PYRb-MVb. The CT peak is more intensive in PYRb-MVb than in PYRb-MVb, in consistency with the stronger CT interaction between PYRb-MVb and MVb\(^{2+}\) from structural analysis. The quenching effect of PYR by MV was observed in the solid-state PL of both PYRb-MVb and PYRb-MVb, indicating the CT interaction between PYRs and MVs (Figure 4c,d).
Figure 3. The calculated atom projected density of states (PDOS) of crystals a) PYRa-MVa and b) PYRb-MVb. The band-projected charge density of the c) topmost occupied band and d) bottom unoccupied band of PYRa-MVa. The isovalue is $1 \times 10^{-3}$ a$_0^{-3}$. e) Calculated isotropic electric conductivity of PYRa-MVa and PYRb-MVb. f) The zoom in conductivity between $-0.7$ and $-0.4$ eV.

Figure 4. Solid-state UV–vis spectra of a) Na$_3$PYRa, MVaCl$_2$, and their 1:1 mixture. b) Na$_3$PYRb, MVbCl$_2$, and their 1:1 mixture. Photoluminescence spectra of c) Na$_3$PYRa and its 1:1 mixture with MVaCl$_2$. d) Na$_3$PYRb and its 1:1 mixture with MVbCl$_2$. The samples are prepared by drop casting 50 μL of 0.01 mM solution on a 1.5 cm × 1.5 cm cover glass pretreated with O$_2$ plasma.
A more efficient quenching was found in \( \text{PYR}_b \)-MV\(_b\) than in \( \text{PYR}_a \)-MV\(_a\), evidenced by the incomplete quenched peak at ca. 700 nm in the 1:1 mixture of \( \text{PYR}_a \)\(^{3-}\) and MV\(_a\)\(^{2+}\) (Figure S8, Supporting Information). This is also caused by the closer packing and stronger CT interaction of \( \text{PYR}_b \)\(^{3-}\) and MV\(_b\)\(^{2+}\) in the crystal structure.

The CT interaction between PYRs and MVs in the aqueous phase is crucial for their functional and structural diversity, thus important to investigate. Besides, the samples are dispersed homogenously in the liquid state, providing more reliable data for quantitative analysis. From UV–vis spectra of the 1:1 mixture of PYRs and MVs at high concentration, a clear characteristic band at ca. 470 nm representing the intermolecular CT was observed as the purple curve shown in Figure 5.[43] We also found that the \( \text{PYR}_b \)\(^{3-}\) itself has a weak intermolecular CT indicated by the weak CT bands at 460 nm as the blue curve shown in the insets of Figure 5b. However, this CT band was inhibited in \( \text{PYR}_a \)-MV\(_a\)/MV\(_b\) complexes (Figure 5; Figure S9, Supporting Information), also indicating a decreased donor ability of \( \text{PYR}_a \)\(^{3-}\) due to the steric effect of the propargyl group. The UV–vis spectra of \( \text{PYR}_a\)- and \( \text{PYR}_b\)-MV\(_b\) complexes are very similar, implying a similar molecular orbital structure.

The electronic excitations of the CTCs were further examined using TD-DFT with a range-separated hybrid functional,
which has been shown to reliably and accurately predict electronic spectra. The calculations show that the band on the low-energy shoulder is a CT excitation. The PYR-MV complex had electronic transition energies of 447 and 361 nm from the ground state to the S1 and S2 excited states, respectively. The electron density difference of the S0 → S1 excitation reveals that electronic charge is shifted from the PYR electron donor to the MV electron acceptor (Figure S10, Supporting Information). The oscillator strength of the CT excitation was weaker than the intramolecular S0 → S1 excitation. The binding energies of 2.10 × 103 m−1 and 7.7 × 103 m−1, consistent with previous findings. We speculate that the extra half acceptor in the crystal structure of PYR-MV contributes to this dynamic quenching process. The maximum emission also blue-shifted dramatically from 430 nm in PYR to 510 nm PYR-MV, which consists of the previously reported amphiphilic pyranines.

2.4. NMR Study of PYR-MV Complexes

For further studying the structures of CTCs in the aqueous phase, we performed the 1H NMR for PYRs, MVs, and their 1:1 mixture in D2O and analyzed the chemical shifts (Figure 6). In Figure 6a,b, we have observed an obvious upfield chemical shifting of 1H on pyrene of PYRs and pyridine of MVs, meaning the shielding effect is mainly from the π...π stacking of the donor.
and acceptor conjugated systems. The high-concentration mixtures of PYRs and MVs have a brown color, which changed dramatically from the original color of PYRs and MVs, indicating strong intermolecular CT interactions between the donors and acceptors.

We can also obtain geometric information on the CTCs from the chemical shifting patterns by plotting the chemical shift of $^1$H located on different parts of the molecules (Figure 6c). In both PYR$_b$-MV$_a$ and PYR$_a$-MV$_b$ complexes, H$_{d1}$ and H$_{d4}$ atoms which are closest to the molecule center of the PYRs and MVs have a larger chemical shift to the upfield due to a stronger shielding effect (−0.54 to −0.58 ppm for H$_{d1}$, −1.09 to −1.22 ppm for H$_{d4}$). There is a very clear trend that the chemical shift values decrease with the increasing distance of $^1$H atoms from the molecule center. In the end, the hydrogens on terminal alkynes (H$_{d3}$ and H$_{d4}$) have an un-shielding effect where the chemical shifts moved slightly to the downfield direction (0.02 for H$_{d3}$, 0.01 for H$_{d4}$). In general, it is most likely that the CTCs of PYRs and MVs were formed via π...π stacking of their conjugated systems with an overlapping molecule center as indicated in Figure 6d. The chemical shifts of H$_{a1}$ and H$_{a4}$ which have similar distances to the molecule center were different in PYR$_{b}$$^+$-MV$_{a}$$^+$ but similar in PYR$_{a}$$^+$-MV$_{b}$$^+$, meaning the PYR$_{b}$$^+$-MV$_{a}$$^+$ complex is more aligned to the molecule center due to its higher symmetry. This observation coincides very well with their crystal structures (Figures 1c and 2c). On the other hand, all the chemical shift values in PYR$_{b}$-MV$_{a}$ complex (hollow circles) are larger than in PYR$_{a}$-MV$_{b}$ complex (hollow squares), indicating a stronger interaction, which is consistent with the results from UV–vis, PL measurements, and DFT calculation. In Figure S11 (Supporting Information), we also studied the chemical shift of PYR$_{b}$-MV$_{a}$ and PYR$_{a}$-MV$_{b}$ complexes. The same trend was observed where the center H atoms have a higher chemical shift.

The derivatives of anthracene are common electron donors in CT pairs. However, in the UV–vis and $^1$H NMR of the mixture of ANT$^+$ and MVs (Figure S12, Supporting Information), no CT band or $^1$H chemical shift was observed, meaning ANT$^+$ (Scheme 1a) lost the electron donor property when introducing a quaternary amino group on the α position. We have also studied the interaction between PYR$_{b}$- and ANT$^+$ as shown in the UV–vis and $^1$H NMR data in Figure 7. In the UV–vis spectra (Figure 7a), there was no obvious CT band in the 1:1 mixture of PYR$_{b}$$^+$ and ANT$^+$ indicating the absence of CT interaction. Although without any color change, we have observed a notable $^1$H chemical shift when mixing PYR$_{b}$- and ANT$^+$ (Figure 7b), caused by the shielding effect from the electrostatic attraction of the oppositely charged molecules. By studying the chemical shift pattern (Figure 7c), we found regions close to H$_{d1}$ and H$_{d4}$ in PYR$_{b}$- and H$_{a1}$ in ANT$^+$ encountered the largest shielding effect as the green shaded area marked in Figure 7d. These areas are likely to overlap due to electrostatic attraction. Our attempt to crystallize PYR$_{b}$$^+$ and ANT$^+$ has failed. These results implied that the opposite charge or the existence of electron donor/acceptor moiety does not necessarily lead to CT interaction between two conjugated systems, implying rational molecular design is important for water-based CTCs.
3. Conclusion

We have determined the crystal structures and obtained the entire range of noncovalent interactions of two submicron-sized crystals (PYR\textsubscript{a}-MV\textsubscript{a} and PYR\textsubscript{b}-MV\textsubscript{b}) using 3DED. Our efforts of combining experiments and DFT calculation also enable us to quantitatively analyze the physical properties in both solid state and aqueous phase. Owing to the various molecular designs, distinct structural topologies and/or symmetries were found in their crystal structures and complexes in the aqueous phase. The different CT intensities in the two complexes lead to various physical properties, e.g., conductivities, CT absorption intensity, PL quenching, etc., which were confirmed experimentally and theoretically in both phases. To be more specific, we have listed the detailed characteristics of the two CT complexes in Table 1. Besides, the spectroscopy study of PYR\textsubscript{b} and ANT\textsuperscript{+} also suggests that electrostatic interaction between conjugated molecules does not adequately allow intermolecular CT.

In summary, we have demonstrated how the structure and properties of crystalline CT materials, especially for small crystals that cannot be investigated by X-ray diffraction, can be investigated by a combination of 3DED, spectroscopy, and DFT calculation. The novel insights into the structure and properties of crystalline CT materials could advance the use of crystal engineering for various applications, i.e., organic electronics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

3D electron diffraction, charge-transfer, crystal, density functional theory, noncovalent interaction

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Table 1. A comparison of major characteristics of PYR\textsubscript{a}-MV\textsubscript{a} and PYR\textsubscript{b}-MV\textsubscript{b} complexes.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>PYR\textsubscript{a}-MV\textsubscript{a}</th>
<th>PYR\textsubscript{b}-MV\textsubscript{b}</th>
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<tr>
<td>Chemical formula</td>
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<td>(C\textsubscript{12}N\textsubscript{2}H\textsubscript{13})(C\textsubscript{16}O\textsubscript{10}S\textsubscript{3}H\textsubscript{7})</td>
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<td>3.50 and 3.76 Å</td>
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<td>PYR\textsubscript{b} to MV\textsubscript{b}</td>
</tr>
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<td>S\textsubscript{0}→S\textsubscript{1}</td>
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<td>−67 kJ mol\textsuperscript{−1}</td>
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<tr>
<td>Experimental conductivity</td>
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<td>&lt;4 × 10\textsuperscript{−7} \text{m} \textsuperscript{−1}</td>
</tr>
<tr>
<td>CT interaction in solid-state</td>
<td>Weaker</td>
<td>Stronger</td>
</tr>
<tr>
<td>CT interaction in the aqueous phase</td>
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<td>D–A pair geometry in the aqueous phase</td>
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<td>Static quenching</td>
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