Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Understanding Dispersive Charge-Transport in Crystalline Organic-Semiconductors

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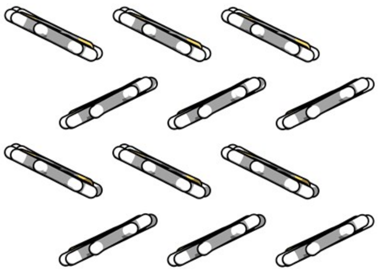
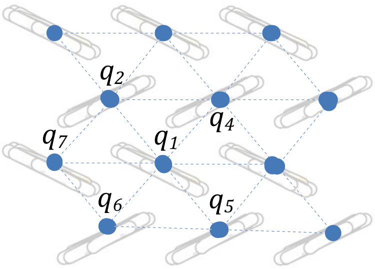
Details of the Charge-transport simulations

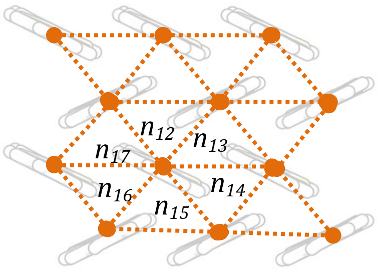


Initial Crystal

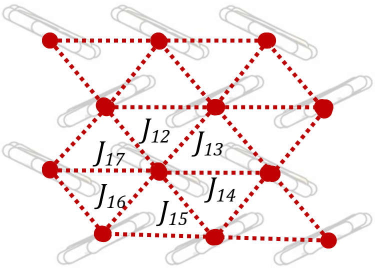


Define hopping sites

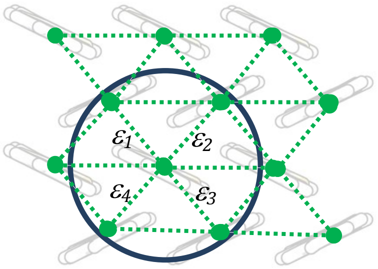
Generate neighborlist (pairs)



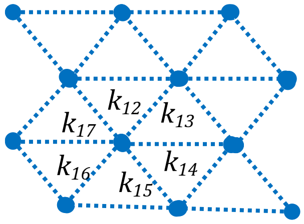
Calculate electronic-coupling between pairs



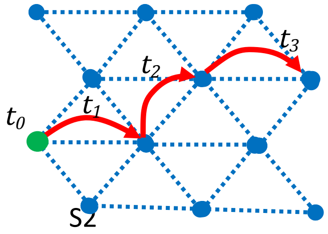
Calculate site-energy for each possible charge-transfer.



Calculate and map hopping sites/rates



Perform kMC simulation



Calculate mobility
μ~d/T

A. Transfer Rates

Here, we use the charge-transport simulations procedure implemented in the **VOTCA** package developed by Prof. Andrienko and co-workers.[S1,S2] The simulations rely on the basis of the assumption that charges are localized on a single molecule and charge-transfer reactions take place *via* an intermolecular hopping. Then the charge-hopping rate can be evaluated by the non-adiabatic Marcus rate[S3,S4]

$$k_{ij} = \frac{J_{ij}^2}{\text{h}}\sqrt{\frac{\pi}{\lambda k_b T}}\exp\left[-\frac{(\Delta E_{ij}-\lambda)}{4\lambda k_b T}\right] \qquad (1)$$

where T is the temperature, J_{ij} is the transfer integral between the initial and final states. λ_e is the electron-transfer reorganization energy and $\Delta E_{ij} = \varepsilon_i - \varepsilon_j$ is called the site-energy difference of the transfer reaction. ε_i is the energy difference of the entire system when molecule i is charged or neutral.

In the next sections we will explain the parameters entering the Marcus rate, Eq. 1.

A. 1. Reorganization Energy:

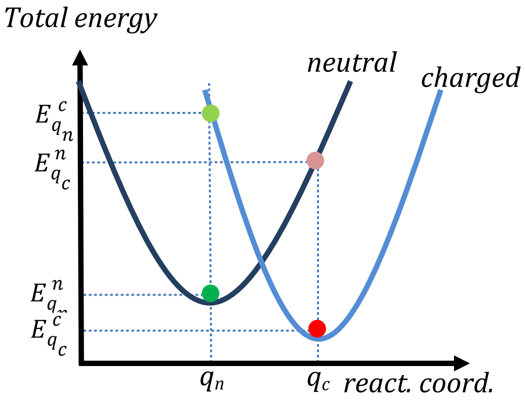


Figure S1. Potential energy surfaces of charged and neutral states along the reaction coordinate. q_n and q_c corresponds to the relaxed (optimized) geometry of the neutral and charged states.

The reorganization energy, λ, has two contributions; intramolecular reorganization energy, λ_{in}, due to non-adiabatic changes in the molecular geometry and the intermolecular reorganization energy, $\lambda_{ext.}$, due to reorganization of the surrounding molecules during the charge-transfer reaction:

$$\lambda = \lambda_{in} + \lambda_{ext} \quad . \qquad (2)$$

Since for organic solids intermolecular reorganization is much slower than the intramolecular reorganization, λ_{ext} is often neglected. Thus, $\lambda \cong \lambda_{in}$.

Intramolecular reorganization, λ, is calculated from adiabatic potential energy surfaces (Figure S1) of neutral and cationic states of compounds, using the following expression:

$$\lambda = \left(E^{n}_{q_c} - E^{n}_{q_n}\right) + (E^{c}_{q_n} - E^{c}_{q_c}) \quad (3)$$

where $E^{n}_{q_n}$ ($E^{c}_{q_n}$) is the energy of the neutral *n* (charged *c*) state of the molecule in its optimized *neutral* geometry and $E^{n}_{q_c}$ ($E^{c}_{q_c}$) is the energy of the neutral *n* (charged *c*) state of the molecule in its optimized *charged* geometry. We used B3LYP/6-311G(d,p)[S5-S8], implemented in Gaussian09, to calculate λ for an isolated molecule.[S9]

Table S1. DFT calculated reorganization energies of five organic materials considered in this study.

	Reorganization Energy, λ (meV)
DNTT	**134**
DCV4T	**228**
NTMTI	**236**
Pentacene	**95**
Rubrene	**160**

A. 2. Site-energies:

A charge-transfer reaction from molecule *i* and *j* is driven by site-energy. Here, we calculate site-energies of the electron transfer from polarizable force-fields with the help of *ab initio* methods. Site-energies include contributions from electrostatic Coulombic interactions (with polarization effects) between atoms and the contributions from the external electric field. Thus, site energy difference is defined as follows:

$$\Delta E_{ij} = \Delta E_{elec.} + \Delta E_{ext.} \quad (4)$$

External electric field contributions are calculated using the expression $\Delta E_{ext.} = q\vec{F}.\vec{d}_{ij}$. Here $\vec{F}$ is the field-vector and $\vec{d}_{ij}$ is the position-vector between molecules *i* and *j*. Polarized Coulombic contributions to site energies are calculated self-consistently using the Thole Model.[S2] Partial charges of neutral and charged states are generated via Merz–Singh– Kollman scheme[S10,S11] using the HF/6-31G(d) method based on B3LYP/6-31G(d,p) [S5-S8] optimized geometries, as implemented in Gaussian09[S9]. Isotropic atomic polarizabilities of the neutral and charged states are reparameterized for each species as to reproduce the molecular polarizabilities obtained from the B3LYP/ 6-311G(d,p) method.[S5-S9]

A. 3. Energetic disorder

Energetic disorder σ is calculated by fitting the histogram of ΔE_{ij} site-energy differences to a Gaussian-distribution function

$$f(\varepsilon,\sigma) = \frac{1}{2\pi} exp[-\frac{\varepsilon^2}{2\sigma^2}] \quad (5)$$

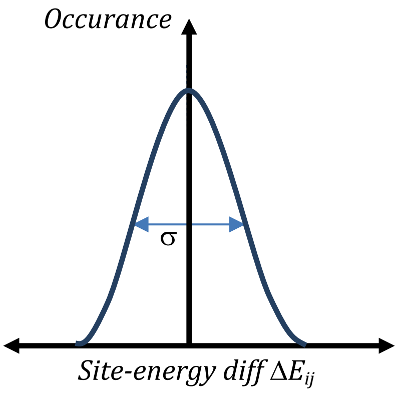


Figure S2. A reprentative graph showing the site-energy difference distribution and its relation to energetic disorder, σ.

B. kMC simulations and electron-mobility:

Charge dynamics is simulated using the kinetic Monte Carlo (kMC) technique using the VOTCA package. In this stochastic procedure, a Markov chain is constructed in site space. A charge-carrier is initially chosen randomly within the space with periodic-boundaries and propagated by hopping between sites, where hopping probabilities (thus the hopping times) from site *i* to a generic site *j* are defined by the Marcus rate, k_{ij}. The total "escape" rate from site *i* to all possible *j* sites is calculated from

$$k_i = \sum_j k_{ij} \qquad (6)$$

from the neighborlist. Thus the probability of hopping from site *i* to a particular site *j* is $p_{ij} = k_{ij}/k_i$. During a kMC run, hopping will occur from *i* to a certain *j* with a higher probability, which is found according to

$$(\sum_{j'}^{j} k_{ij'})/k_i \le u_1 \qquad (7)$$

where, u_1 is a uniform random number between 0 and 1. Then the event is carried out and charge is moved from site *i* to *j* and the time is updated, $t = t + \Delta t$, where

$$\Delta t = ln(1/u_2)/k_i \, , \qquad (8)$$

where, u_2 is another uniform random number. The simulations are performed until the results are converged. Charge-carrier mobility is then calculated by

$$\mu = \frac{v}{|F|},$$

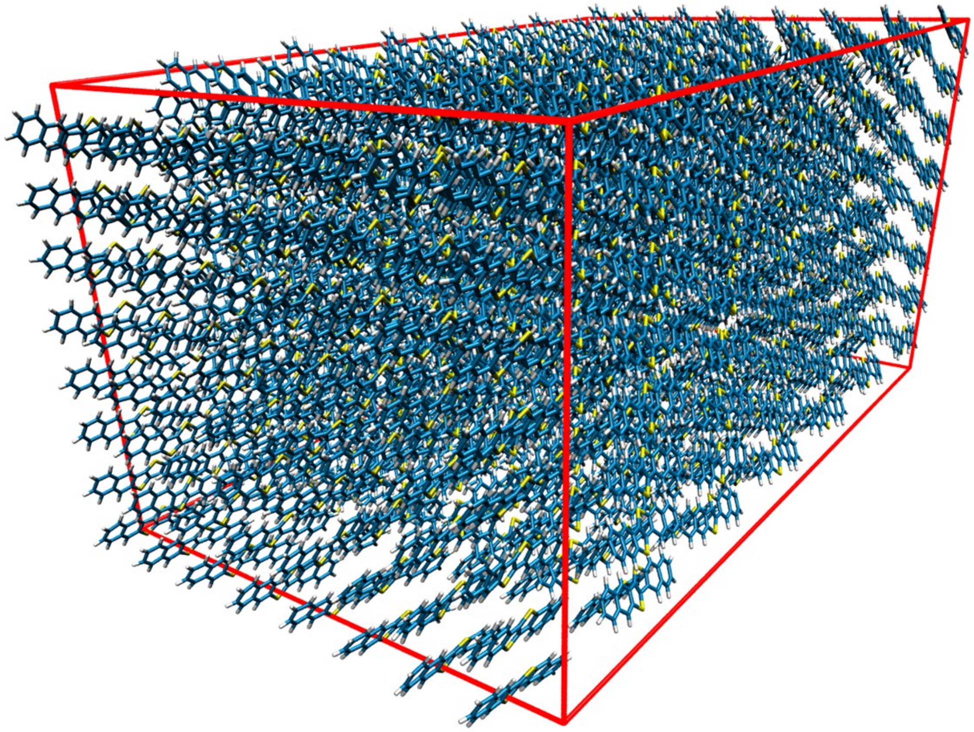
where v is the charge-carrier velocity and F (=10^7 V/m) is the applied electric field. The reported mobilities are the averages over 10-100 stochastic realizations.

Table S2. References for the cif of the crystal structures.

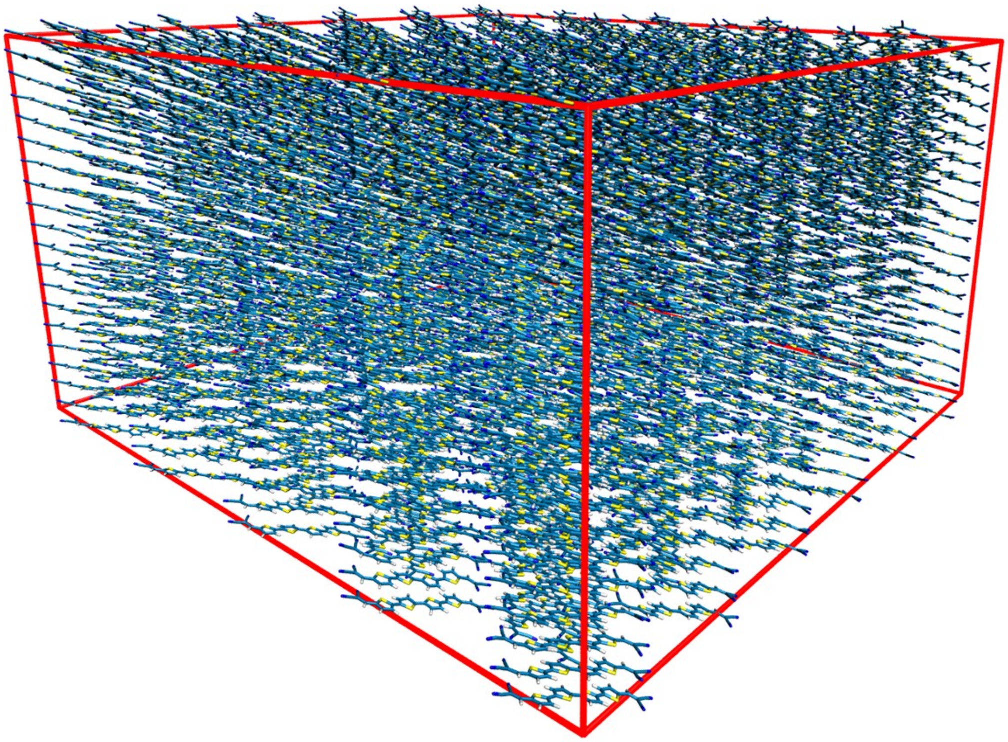
	Reference	Guidance to download
DNTT	T. Yamamoto and K. Takimiya *J. Am. Chem. Soc.*, 2007, **129**, 2224– 2225.	downloadable at the SI of the reference.
DCV4T	R. Fitzner, E. Reinold, A. Mishra, E. Mena-Osteritz, H. Ziehlke, C. Körner, K. Leo, M. Riede, M.; Weil, O. Tsaryova, A. Weiss, C. Uhrich, M.; Pfeiffer and P. Bauerle *Adv. Funct. Mater.*, 2011, **21**, 897– 910.	Deposited to Cambridge Crystallographic Database (CCDC) with the code number 786021.
NTMTI	E. M. García-Frutos, E. Gutierrez-Puebla, M. Monge, E. Ramírez, P. d. Andrés, A. d. Andrés, R. Ramírez and B. Gómez-Lor, *Org. Electron.*, 2009, **10**, 643– 652	Deposited to Cambridge Crystallographic Database (CCDC) with the code number 670066.
Pentacene	H. Yoshida, K. Inaba and N. Sato, *Appl. Phys. Lett.* 2007, **90**, 181930.	downloadable at http://webcsd.ccdc.cam.ac.uk/ with the CSD identifier “PENCENXX”
Rubrene	O. D. Jurchescu, A. Meetsma and T. T. M. Palstra, *Acta Crystallogr. Sect. B: Struct. Sci.* 2006, **62**, 330.	downloadable at http://webcsd.ccdc.cam.ac.uk/ with the CSD identifier “QQQCIG11”

Table S2. High-quality images of supercells.

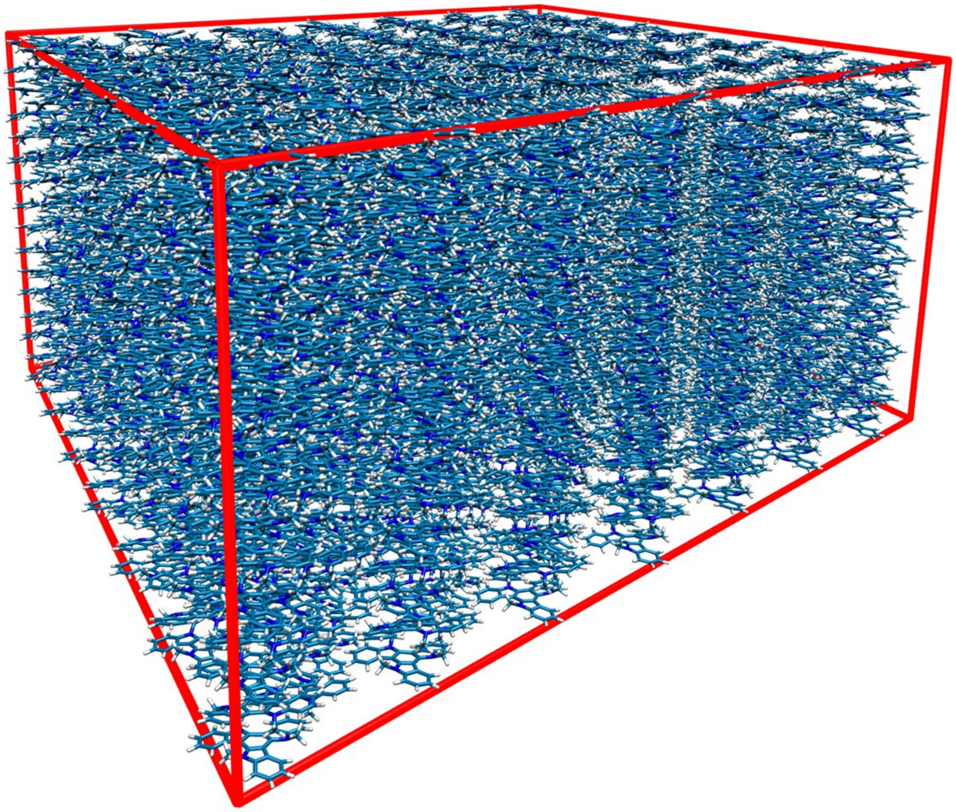
DNTT



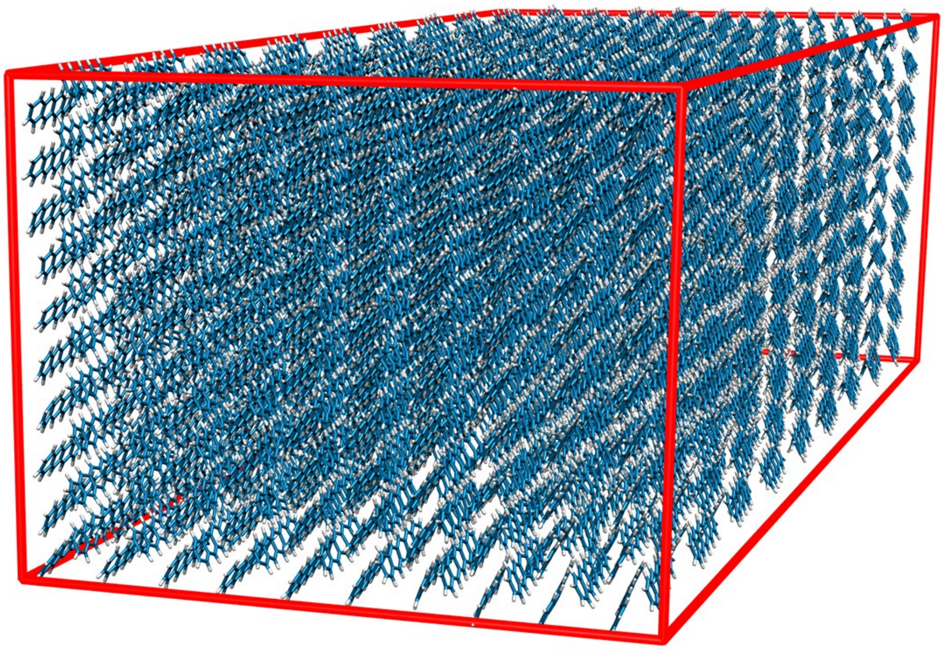
DCV4T



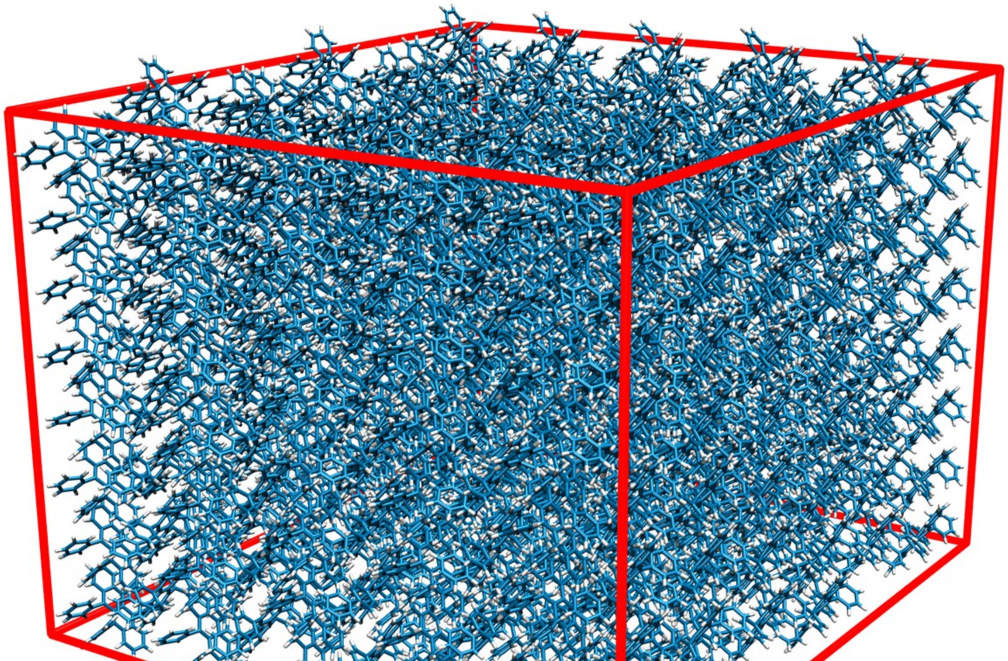
NTMTI



Pentacene



Rubrene



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[S2] V. Ruehle, A. Lukyanov, F. May, M. Schrader, T. Vehoff, J. Kirkpatrick, B. Baumeier and D. Andrienko, *J. Chem*. *Theory Comput*., 2011, **7**, 3335−3345.

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[S9] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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