Supplementary Information

for

How does alkyl chain length modify the properties of triphenylamine-based hole

transport materials?

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1. Computational Details

Quantum chemistry computations

All the geometries of the neutral and cationic molecules were optimized using B3LYP-^{1,2}D3BJ³ in conjunction with the 6-31G(d,p) all-electron basis set. Computations related to the following section were performed with Gaussian09.⁴ The ionization potentials (IPs) were computed using a Δ SCF (delta self-consistent field) procedure in conjunction with different density functionals and the 6-31G(d,p) basis set (Table S1):

$$IP = \Delta SCF = E_{\rm cN} - E_{\rm nN} \tag{1}$$

where E_{nN}/E_{cN} is the total energy of the neutral/charged molecule in the neutral geometry. The UV-vis absorption spectra were computed at the TD-B3LYP/6-31G(d,p) level with the conductor-like polarized continuum (C-PCM)⁵ solvent model using tetrahydrofuran. Gaussian broadening with a 0.20 eV σ was adopted to generate the absorption spectrum.

Amorphous Structure Construction

The amorphous assemblies were constructed from a unit cell containing 64 molecules using Packmol.⁶ The molecules were first minimized using the conjugate gradient algorithm and then equilibrated in the NPT ensemble (700K, 1bar) by performing a classical molecular dynamics (MD) simulation. The equilibrated system was then extended to a 2x2x2 supercell with 512 molecules. Further equilibration (700K, 1bar) was performed for 5 ns. Finally, a 10 ns equilibration in the NPT ensemble (300K, 1bar) followed by another 10 ns of production run served to generate 1000 snapshots. The simulations were performed under periodic boundary conditions using the GROMACS package^{7,8,9} and the CGenFF^{10,11} force field along with charges obtained by the restrained electrostatic potential (RESP)¹² procedure based on HF/6-31G(d,p). The temperature and pressure control used velocity rescaling with a stochastic term¹³ (T = 300K, τ_T = 1.0 ps) and an isotropic coupling for the pressure from a Berendsen barostat (P₀ = 1 bar, $\chi = 4.5 \times 10^{-5}$ bar⁻¹, $\tau_P = 1.0$ ps). The time step used in all simulation was 1 fs. Bonds involving H atoms were constrained using Linear Constraint Solver (LINCS) algorithm. A cutoff of 12 Å was applied to the van der Waals interaction through the force-switch mode. As for electrostatic interactions, the particle mesh Ewald (PME) method was employed with a 0.12 nm Fourier spacing.

Hole Mobility Computations

The hole mobilities of the HTMs were computed according to the semi-classical Marcus charge-transfer theory on 200 frames extracted from previous MD trajectories using the VOTCA package.^{14,15} Within this formalism, the charges are assumed to be localized on a single molecule (*i.e.*, on a single π -conjugated core) with each core being considered as a hopping site. The charge transfer process occurs by hopping between the different sites with the hopping rate calculated using equation (1) in the main article. The reorganization energy was computed by a 4-point method at the B3LYP-D3BJ/6-31G(d,p) level:

$$\lambda = E_{\rm nC} - E_{\rm nN} + E_{\rm cN} - E_{\rm cC} \tag{2}$$

where E_{nN} (E_{cC}) is the total energy of the neutral (charged) molecule in the neutral (charged) geometry and E_{nC} (E_{cN}) is the energy of the neutral (charged) molecule in the charged (neutral) geometry. The Thole model was used to compute site energies (E_i or E_j), which include contributions from electrostatic interactions, polarization and external electric field.¹⁵ The atomic multipoles needed by this model for the neutral and charged states were generated using the GDMA technique.¹⁶ The transfer integrals (J_{ij}) were computed using Zerner's independent neglect of differential overlap (ZINDO)^{15,17} for every molecular pair *ij* in the neighbor list. This list was established for every molecular pair naving a distance between their nearest fragments within 7 Å. Once all the parameters necessary to calculate the hopping rate are computed, a 1 ms kinetic Monte Carlo (KMC) simulation was performed using a 10⁵ Vcm⁻¹ electric field to obtain the hole mobility. For a given snapshot (structure), the KMC simulations were conducted with the electric field in the three different directions resulting in a total simulation time that corresponds to three times the number of snapshots. The final hole mobility is obtained through averaging all the mobilities of 600 KMC simulations.

Water Contact Angle

We employed the soft-confined method to create an amorphous organic solid surface preventing uncontrollable roughness at the surface.¹⁸ Starting from a supercell with x=y=155.0580 Å and z=310.1160 Å, two xenon crystal walls were placed 120 Å apart. Using Packmol, 512 molecules were then inserted between these two walls forming a sandwich structure. The NVT simulation was then performed at 500K, while gradually decreasing the distance between the two walls until reaching the targeted

density for the middle amorphous slabs. For each given specie, the targeted density was chosen as the bulk density of the amorphous phase. Once the desired density was reached, the system was equilibrated in the NVT ensemble at 300K for 10 ns with fixed walls. Finally, the xenon walls were removed, leaving the amorphous slab ready for further simulations.

The water droplet placed atop the amorphous slab was created from a water cube with 1500 water molecules and equilibrated in the NPT ensemble (300K, 1bar) using the simple point charge model (SPC).¹⁹ This equilibrated cube was then placed into a 110 Å side cubic supercell and equilibrated in the NVT ensemble at 300K to obtain a water droplet. This droplet was deposited on the amorphous slab and equilibrated in the NVT ensemble at 300K with fixed slab for 10 ns. The simulation details are similar to the *Amorphous Structure Construction* section. The Particle Mesh Ewald approach with the slab correction 3dc was adopted to compute the long-range Coulombic interactions.²⁰

Oxygen Diffusion

We took the amorphous matrix from the last configuration of the trajectory of the simulation in the *Amorphous Structure Construction* step for each molecule. For each simulation cell, five O_2 molecules were randomly inserted into the amorphous matrix using Packmol.⁶ The structures were first minimized using the conjugate gradient algorithm and then equilibrated in the NVT ensemble (300K). The methods employed for the thermal coupling are the same as in the *Amorphous Structure Construction* section. After the equilibrium state was reached, a 20 ns production run was performed with the same ensemble for each cell. In order to obtain statistically meaningful results, 10 MD simulations with different initial O_2 positions have been performed, creating 50 O_2 trajectories for each TPAF-R molecule.

2. Electronic Properties

IP Computation with Different Density Functionals

IPs computed using different density functional approximations are listed in Table S1. The results obtained from different methods show the same trend: IPs do not change significantly with the chain length. For all functionals considered here, the IPs are higher than the experimental ones, but the trends are identical. Since only the IP trends of the different chain length are considered, the results remain insightful.

Table S1. Ionization potentials (eV) at the different levels using the 6-31G(d,p) basis set .

	Ethyl	Butyl	Hexyl	Octyl	Decyl
B3LYP	5.67	5.65	5.64	5.63	5.63
PBE0	5.82	5.80	5.78	5.78	5.78
M06-2X	6.22	6.21	6.20	6.20	6.20
ωB97X-D	6.16	6.13	6.13	6.13	6.14
Exp.	5.2 ²¹	5.2 ²¹	5.2 ²¹	_	_

Absorption Spectra

The absorption spectra are computed at the TD-B3LYP/6-31G(d,p) level (Figure S1). Because the introduction of long alkyl chain has a negligible effect on the distortion of the π -conjugated moiety, the absorption spectrum for the TPAF-R featuring different alkyl chain lengths are nearly the same.



Figure S1. Computed UV-visible absorption spectra of each molecule at the TD-B3LYP/6-31G(d,p) level.

3. Transport Properties

The source of disorder can be partitioned into dynamic and static (positional) disorders, as shown in scheme S1.²²



Scheme S1. Classification of disorder in amorphous organic materials.

Dynamic Disorder

To evaluate the time variation of the squared of the transfer integrals (J^2) and the site energy differences (ΔE_{ij}) , we compute the standard deviation $(\sigma_J^2 \text{ and } \sigma_{\Delta E} [\sigma_D \text{ in the main text}])$ and average $(\langle J^2 \rangle$ and $\langle \Delta E \rangle)$ of these properties for each pair of molecules (sites) along the MD trajectory, as shown in Figure S2 (a) and S3. One observes both the spreading of $\langle J^2 \rangle$, which originates from the static disorder, and the magnitude of the fluctuation (σ_J^2) growing with increasing $\langle J^2 \rangle$. In order to avoid the interference from the static disorder, we introduce a coefficient of variation (C_J^2) quantifying the degree of fluctuation with respect to its average value defined as:

$$C_{\rm V} of J^2 \equiv C_{\rm J^2} = \frac{\sigma_{\rm J^2}}{\langle J^2 \rangle}$$
 (3)

From Figure S2(b), C_J^2 shows much a smaller dependence on $\langle J^2 \rangle$ and can thus serve

as a good descriptor of the degree of fluctuation of J^2 . On the other hand, a spread of $\langle \Delta E \rangle$ originating from the static disorder is also present (Figure S3(a)). Unlike σ_J^2 , $\sigma_{\Delta E}$ exhibits very little dependence on $\langle \Delta E \rangle$, indicating that it does characterize the dynamic energetic disorder free from the effect of static disorder.

Note that the internal energy is not included in our computed site energy, because the internal energetic disorder is usually very small compared to total energetic disorder (σ_T) .²³ Therefore, the dynamic energetic disorder presented here purely originates from the fluctuations of the intermolecular interactions (environment effects). For the sake of consistency, the dynamic disorder resulting from internal energy fluctuation ($\sigma_{D,int}$) was evaluated using the following equation:²²

$$\sigma_{D,int} = \sqrt{\lambda k_B T} \tag{4}$$

where k_B is the Boltzmann constant, λ is the reorganization energy and T is the temperature. Due to a similar reorganization energy for all molecules, their $\sigma_{D, int}$ have no sizable difference. Overall, these two dynamic energetic disorders [$\sigma_{\Delta E}$ and $\sigma_{D, int}$] show no sizable change with the chain length (Figure S3(b)), and suggest that alkyl chain length has a negligible effect on the dynamic energetic disorder for TPAF-R.



Figure S2. (a) Standard deviation of J^2 vs. average of J^2 plot. (b) Coefficient of variation of J^2 vs. average of J^2 plot.



Figure S3. Standard deviation of ΔE vs. average of ΔE plot.

In order to investigate the degree of flexibility of a given moiety, we introduce the root mean square fluctuation (RMSF), defined as:

$$RMSF_{M} = \sum_{i=1}^{N_{M}} \sqrt{\langle \left(r_{i,t} - \overline{r_{i}}\right)^{2} \rangle / N_{M}}$$
(5)

where RMSF_M is the root mean square fluctuation of moiety M, $r_{i,t}$ is the position of atom *i* at time *t*, $\overline{r_i}$ is the time-average position of atom *i* and N_M is the number of atoms in moiety *M*.

Static Disorder

Given that the static and dynamic disorder both exist in each snapshot of the MD trajectory,²² we need a measure to evaluate the contribution arising from the static contribution. To the best of our knowledge, there is no ideal way to extract the positional static disorder from an MD trajectory. However, since the standard deviation of J^2 with respect to its average value is only ~200% for each molecule pair, the total disorder of J^2 possessing a wide spread of distribution ($C_J^2 > 900\%$) is mainly determined by the static disorder. Thus, we approximated positional disorder with the total disorder of transfer integral.

The static energetic disorder (σ_s) is computed using the following equation:²²

$$\sigma_S^2 = \sigma_T^2 - \sigma_D^2 \tag{6}$$

where σ_T , σ_S and σ_D are the total, static and dynamic energetic disorder, respectively. Total energetic disorder is evaluated by taking standard deviation of site energy difference over all pairs of sites in a snapshot (ensemble average).

The dipole moments used in the correlated Gaussian disorder model (CDM) were

computed at the DFT B3LYP/6-31G(d,p) level. The lattice spacing (*a*) also needed in the CDM is approximated as:

$$a = \sqrt[3]{\frac{V}{N}} \tag{7}$$

where V is the amorphous cell volume in the MD simulation and N the number of molecules in the cell. The results are tabulated in Table S2.

-	-				
	Ethyl	Butyl	Hexyl	Octyl	Decyl
d (Debye)	1.30	1.40	1.42	1.43	1.43
a (nm)	1.15	1.23	1.29	1.35	1.41
d/a ² (Debye/nm ²)	0.99	0.92	0.85	0.78	0.73

Table S2. Computed dipole moment (Debye) and lattice spacing (nm).

4. Water Contact Angle

Scheme S2 illustrates the simulation process for obtaining the water contact angle (WCA). The WCA is estimated by post-processing the information taken from the MD trajectory. There exist different methods to extract the water contact angle from a molecular dynamics (MD) trajectory.^{18,20,24–27} Herein, we adopted the approach reported by Liu *et al.*¹⁸, which consists in obtaining the radius of water droplet at each z coordinate r(z) by:

$$\pi r^2 \Delta z \rho = \Delta m \Longrightarrow r(z) = \sqrt{\frac{1}{\rho \pi} \times \frac{\Delta m(z)}{\Delta z}}$$
 (8)

Near the substrate, the density of the water droplet dramatically oscillates due to the surface effect (see r(z) in Figure S4). We thus evaluated the WCA after removal of this fluctuating region.¹⁸ The water contact angle was obtained by first fitting the z-r(z) curve with n^{th} degree polynomial and then taking the derivative to find the slope (angle). We fitted the curve using polynomials of 2^{nd} to 12^{th} degrees and found a fluctuation around a fixed value since 7^{th} degree. The WCA for each species were then obtained by taking the average of the values obtained from 7^{th} to 12^{th} degree polynomial fitting.



Scheme S2 Illustration of the simulation procedure for the water contact angle computation.



Figure S4. Radius of the water droplet as a function of the droplet height r(z).

5. Oxygen Diffusion

To investigate the effect of chain length on O2 diffusion, we calculate the diffusion constants (D) of O_2 by means of Einstein's relation:

$$D = \lim_{t \to \infty} \frac{\langle r^2 \rangle}{6t} \tag{9}$$

where $\langle r^2 \rangle = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ is the mean square displacement (MSD) of the center of mass of the O₂ molecule extracted from the MD trajectory. Since the MSD function obtained from a single MD trajectory of a particle diffusing in amorphous solid or liquid is usually very noisy and deviates from linearity within an acceptable time scale, we average all the MSD functions of the 50 different O₂ trajectories and then extracted the diffusion constant from slope fitting of the averaged MSD at the long time limit (Figure S5(a)(b)). The free volume (V_{Free}) is evaluated by calculating the difference between total cell volume and the volume occupied by molecular VDW volume (VDW radii are taken from Bondi's work²⁸) using GROMACS (gmx freevolume).



Figure S5. (a) Illustration of a simulation cell: amorphous matrix and 50 different O_2 initial positions. (b) Characteristic of the RMSD for trap-free (red line) and trapped (green line). (c) MSD and fitted slope at long time limit for each case.

In order to understand what happens during diffusion process, we compute root mean square displacement (RMSD) of O₂, defined as:

$$RMSD(t) = \sqrt{\frac{1}{2}\sum_{i=1}^{2} |\boldsymbol{r}_{0i}(t) - \boldsymbol{r}_{0i}(0)|^2}$$
(10)

where $\mathbf{r}_{Oi}(t)$ is the position of oxygen atom *i* at time *t*. The computed results are shown in Figure S6 to Figure S15. As shown in Figure S5(c), we identified different diffusion patterns based on the RMSDs, such as trap-free and trapped behavior.



Figure S6. RMSD of TPAF-E for simulations 1 to 6.



Figure S7. RMSD of TPAF-E for simulations 7 to 10.



Figure S8. RMSD of TPAF-B for simulations 1 to 6.



Figure S9. RMSD of TPAF-B for simulations 7 to 10.



Figure S10. RMSD of TPAF-H for simulations 1 to 6.



Figure S11. RMSD of TPAF-H for simulations 7 to 10.



Figure S12. RMSD of TPAF-O for simulations 1 to 6.



Figure S13. RMSD of TPAF-O for simulations 7 to 10.



Figure S14. RMSD of TPAF-D for simulations 1 to 6.



Figure S15. RMSD of TPAF-D for simulations 7 to 10.

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