Supporting Information

Effect of the electron donating group on excited-state electronic nature and epsilon-
near-zero properties of curcuminoid-borondifluoride dyes

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1. Table of spectroscopic data and photophysical properties

Absorption spectra was measured on Hitachi spectrophotometer U-3900, a double beam single monochromator system. Fluorescence spectra was measured on Horiba Jobin Yvon fluorimeter FluoroMax-4.

Table S1. Spectroscopic data and photophysical properties of compounds 1, 2 and 3 in solvents of different polarity at room temperature

| solvent    | 1     | 2     | 3     | 4     | 5     | 6     |
|------------|-------|-------|-------|-------|-------|-------|
|            | λ_{abs} | λ_{em} | Δν_{ST} | λ_{abs} | λ_{em} | Δν_{ST} | λ_{abs} | λ_{em} | Δν_{ST} |
| Cyclo      | 514    | 540   | 937    | 560    | 583   | 704    | 612    | 639   | 690    |
| CCl₄       | 522    | 558   | 1236   | 565    | 601   | 1060   | 626    | 665   | 937    |
| Bu₂O       | 511    | 585   | 2475   | 564    | 614   | 1444   | 622    | 668   | 1107   |
| Et₂O       | 506    | 607   | 3288   | 562    | 635   | 2046   | 624    | 673   | 1167   |
| Chloroform | 524    | 652   | 3747   | 593    | 698   | 2537   | 661    | 731   | 1449   |
| BuOAc      | 507    | 642   | 4148   | 567    | 657   | 2416   | 631    | 690   | 1355   |
| EtOAc      | 504    | 668   | 4871   | 568    | 677   | 2834   | 636    | 699   | 1417   |
| DCM        | 516    | 709   | 5275   | 595    | 735   | 3201   | 665    | 749   | 1686   |
| DCE        | 519    | 716   | 5301   | 594    | 732   | 3174   | 665    | 750   | 1704   |
| Acetone    | 507    | 763   | 6618   | 580    | 730   | 3543   | 651    | 729   | 1644   |
| ACN        | 507    | 805   | 7302   | 583    | 770   | 4166   | 661    | 756   | 1901   |

*Absorption maximum wavelengths λ_{abs} (nm). Fluorescence maximum wavelengths λ_{em} (nm). Stokes shifts Δν_{ST} (cm⁻¹). Cyclo: Cyclohexane. CCl₄: Carbon tetrachloride. Bu₂O: n-Dibutylether. Et₂O: Diethyl ether. BuOAc : n-Butylacetate. EtOAc: Ethyl acetate. DCM: Dichloromethane. DCE: 1.2-Dichloroethane. ACN: Acetonitrile.
Table S2. Spectroscopic data and photophysical properties of compounds 4, 5 and 6 in solvents of different polarity at room temperature\(^a\)

| solvent     | \(\lambda_{\text{abs}}\) (nm) | \(\lambda_{\text{em}}\) (nm) | \(\Delta \nu_{ST}\) (cm\(^{-1}\)) | \(\lambda_{\text{abs}}\) (nm) | \(\lambda_{\text{em}}\) (nm) | \(\Delta \nu_{ST}\) (cm\(^{-1}\)) | \(\lambda_{\text{abs}}\) (nm) | \(\lambda_{\text{em}}\) (nm) | \(\Delta \nu_{ST}\) (cm\(^{-1}\)) |
|-------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Cyclo       | 562              | 575              | 402              | 594              | 606              | 333              | 620              | 637              | 430              |
| CCl\(_4\)   | 574              | 601              | 783              | 610              | 630              | 520              | 633              | 659              | 623              |
| Bu\(_2\)O   | 574              | 602              | 810              | 608              | 640              | 901              | 636              | 666              | 708              |
| Et\(_2\)O   | 576              | 616              | 1127             | 609              | 641              | 820              | 640              | 675              | 810              |
| Chloroform  | 609              | 677              | 1649             | 643              | 684              | 932              | 682              | 729              | 945              |
| BuOAc       | 586              | 641              | 1464             | 625              | 655              | 733              | 655              | 693              | 837              |
| EtOAc       | 591              | 651              | 1559             | 625              | 661              | 871              | 660              | 701              | 886              |
| DCM         | 620              | 698              | 1802             | 649              | 694              | 999              | 692              | 742              | 974              |
| DCE         | 620              | 702              | 1884             | 651              | 696              | 993              | 695              | 744              | 948              |
| Acetone     | 609              | 689              | 1907             | 641              | 683              | 959              | 681              | 726              | 910              |
| ACN         | 618              | 713.5            | 2166             | 652              | 697              | 990              | 696              | 748              | 998              |

\(^a\) Absorption maximum wavelengths \(\lambda_{\text{abs}}\) (nm). Fluorescence maximum wavelengths \(\lambda_{\text{em}}\) (nm). Stokes shifts \(\Delta \nu_{ST}\) (cm\(^{-1}\)). ;
Cyclo: Cyclohexane. CCl\(_4\): Carbon tetrachloride. Bu\(_2\)O: n-Dibutylether. Et\(_2\)O: Diethyl ether. BuOAc: n-Butylacetate. EtOAc: Ethyl acetate. DCM: Dichloromethane. DCE: 1,2-Dichloroethane. ACN: Acetonitrile.

Table S3. Dielectric constant (\(\varepsilon\)), refractive index (\(n\)) and orientation polarizability (\(\Delta \Gamma\)) of 11 solvents.

|                | Cyclohexane (Cyclo) | Carbon tetrachloride (CCl\(_4\)) | n-Dibutylether (Bu\(_2\)O) | Diethyl ether (Et\(_2\)O) | Chloroform (CHCl\(_3\)) | n-Butylacetate (BuOAc) |
|----------------|---------------------|----------------------------------|---------------------------|---------------------------|--------------------------|-------------------------|
| \(\varepsilon\) | 2.02                | 2.24                             | 3.1                       | 4.33                      | 4.81                     | 5.07                    |
| \(n\)          | 1.426               | 1.416                            | 1.399                     | 1.352                     | 1.443                    | 1.392                   |
| \(\Delta \Gamma\) | 0.1, 0.118            | 0.196                            | 0.251                     | 0.251                     | 0.269                    |
|                | Ethyl acetate (EtOAc) | Dichloromethane (DCM) | Dichloroethane (DCE) | Acetone | Acetonitrile (ACN) |
| \(\varepsilon\) | 6.02 | 8.93 | 10.5 | 20.7 | 37.5 |
| \(n\)          | 1.372 | 1.424 | 1.445 | 1.359 | 1.344 |
| \(\Delta \Gamma\) | 0.292 | 0.319 | 0.326 | 0.374 | 0.393 |
2. Cyclic voltammetry data

Cyclic voltammetry (CV) data were acquired using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A three-electrode system with a Pt working electrode (diameter 1.6 mm), a Pt counter electrode and a Ag/AgCl (with a 3 M NaCl filling solution) reference electrode was used. (n-Bu)$_4$NPF$_6$ (0.1 M CH$_2$Cl$_2$) served as an inert electrolyte. Cyclic voltammograms were recorded at a scan rate of 100 mV s$^{-1}$ for solution of dyes at a concentration of ca. 10$^{-3}$ M. Ferrocene was used as an internal standard.

Figure S1 | Cyclic voltammograms of 1 (a/), 3 (b/), 4 (c/), 5 (d/) and 6 (e/) in dichloromethane solution containing 0.1 M of (n-Bu)$_4$NPF$_6$ (scan rate of 100 mV s$^{-1}$).
3. Solvatochromism of polymethine model squaraine

Molecular structure of polymethine model squaraine is shown in Figure S2, named as compound 7.

![Figure S2](image)

**Figure S2** | Molecular structure of polymethine model squaraine, compound 7.

Solvatochromism of compound 7 is shown in Figure S3.

![Figure S3](image)

**Figure S3** | Solvatochromism of polymethine model squaraine 7. (a) and (b) show spectra of normalized absorption and normalized photoluminescence in 7 solvents with different polarity, namely, Cyclohexane (Cyclo), Bu₂O (dibutyl ether), Diethyl ether (Et₂O), Ethyl acetate (EtOAc), Dichloromethane (DCM), Acetone, Acetonitrile (ACN). (c) shows Stokes shift. (d) is the Lippert-Mataga plot of compound 7.
4. Grazing incidence wide angle x-ray scattering (GIWAXS)

Figure S4 | GIWAXS pattern (a/, c/ and e/) and the corresponding radial profile (b/, d/ and f/) of compound 1 (a/ and b/), 2 (c/ and d/) and 3 (e/ and f/).

The GIWAXS pattern (Fig S4 a/) and the corresponding radial profile (Fig S4 b/) of the pristine 1 film display coexistence of two phases: i) an amorphous phase (two broad scattering rings with maximums at \( q = 0.8 \) and 1.4 Å\(^{-1}\), for average lateral distances \( h_1, h_2 = 2\pi/q = 7.8, 4.5 \) Å) and ii) a lamellar crystalline phase (orders (00l) of the lamellar periodicity \( d = 40.5 \) Å and reflections (hk0) and (hkl) of the in-plane arrangement and the three-dimensional structure). There is naturally no orientation of amorphous domains, while the crystalline domains adopt orientations with lamellae parallel to substrate.
The GIWAXS pattern (Fig S4 c/) and the corresponding radial profile (Fig S4 d/) of the pristine 2 film reveal an amorphous film, giving rise to broad rings from lateral distances between segments ($h_1, h_2 = 6.6, 4.5\ \text{Å}$), and a broad small-angle ring from packing of entire molecules ($D = 17\ \text{Å}$). The GIWAXS pattern (Fig S4 e/) and the corresponding radial profile (Fig S4 f/) of the pristine 3 film reveal an amorphous film, giving rise to broad rings from lateral distances between segments ($h_1, h_2 = 6.3, 4.5\ \text{Å}$), and a broad small-angle ring from packing of entire molecules ($D = 17\ \text{Å}$).

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**Figure S5** GIWAXS pattern (a/, c/ and e/) and the corresponding radial profile (b/, d/ and f/) of compound 4 (a/ and b/), 5 (c/ and d/) and 6 (e/ and f/).
The GIWAXS pattern (Fig S5 a/) and the corresponding radial profile (Fig S5 b/) of the pristine film reveal an amorphous film, giving rise to broad rings from lateral distances between segments \( (h_1, h_2 = 6.6, 4.3 \, \text{Å}) \), and a broad small-angle ring from packing of entire molecules \( (D = 16 \, \text{Å}) \).

The GIWAXS pattern (Fig S5 c/) and the corresponding radial profile (Fig S5 d/) of the pristine film reveal an amorphous film, giving rise to only two broad rings, with maximums at \( q = 1.1 \) and \( 1.6 \, \text{Å}^{-1} \) \( (h_1, h_2 = 5.6, 4.0 \, \text{Å}) \) from lateral distances between molecular segments.

The GIWAXS pattern (Fig S5 e/) and the corresponding radial profile (Fig S5 f/) of the pristine film display a smectic like structure with two sharp orders of a lamellar periodicity \( (d = 16.3 \, \text{Å}) \) generated by the alternation of aliphatic chain and aromatic core layers, besides broad rings from liquid-like lateral distances within layers \( (h_2 = 4.3 \, \text{Å}) \). The reflections align onto the meridian, which indicates that lamellae are oriented parallel to substrate. A continuous broad ring \( (D = 14 \, \text{Å}) \) moreover appears in the small-angle region, due to the liquid-like molecular packing within amorphous domains that coexist with the mesomorphic domains.
5. Spectroscopic ellipsometry measurement

The alpha SE spectroscopic ellipsometer was used at incident angle 70° to measure $\Psi$ and $\Delta$ of the thin film from 380nm to 900nm. The rotating polarizer, photo-elastic modulator modulates between P-pol and S-pol from which the reflection ratio provides the information to unravel the dielectric index values of the thin films through Fresnel coefficient calculation. See Figure 5 for the dielectric permittivity spectra of all the six Curc series films. See Figures S6 for $\Psi$ and $\Delta$ measurement and fitted data. See Figure S7 for the refractive index $n$ and absorption coefficient $k$ of all the six Cure series films. Model fitting parameters of the measured data are shown in Table S4 to 11. Each film is fitted from a substrate/transparent thin film/air model. Fitting is conducted through the sum of oscillator functions such as Gaussian and Tauc-Lorentz oscillators.

![Figure S6](image1)

**Figure S6** Measured $\Psi$, black, and $\Delta$, red, spectroscopic ellipsometry data and fitted model, dashed blue of six Curc series films.
Figure S7: Refractive index $n$ (solid curve) and absorption coefficient $k$ (dashed curve) of all the six Curc series films are plotted. In (a) and (f) black and red curves correspond to ordinary and extra-ordinary components.

Table S4. Oscillator list for in-plane compound 1 dielectric permittivity

| Number | Type   | Amplitude | Broadening | Center energy |
|--------|--------|-----------|------------|---------------|
| 1      | Gaussian | 0.559     | 0.204      | 2.149         |
| 2      | Gaussian | 1.400     | 0.204      | 2.216         |
| 3      | Gaussian | 1.181     | 0.260      | 2.366         |
| 4      | Gaussian | 0.966     | 0.346      | 2.547         |
| 5      | Gaussian | 0.502     | 0.508      | 2.971         |
| 6      | Gaussian | 1.089     | 1.288      | 4.325         |
**Table S5.** Oscillator list for out-of-plane compound 1 dielectric permittivity

| Number | Type      | Amplitude | Broadening | Center energy |
|--------|-----------|-----------|------------|---------------|
| 1      | Gaussian  | 0.523     | 0.208      | 2.150         |
| 2      | Gaussian  | 1.421     | 0.195      | 2.193         |
| 3      | Gaussian  | 1.258     | 0.257      | 2.361         |
| 4      | Gaussian  | 0.975     | 0.330      | 2.531         |
| 5      | Gaussian  | 0.572     | 0.608      | 2.923         |
| 6      | Gaussian  | 0.550     | 0.576      | 3.823         |

**Table S6.** Oscillator list for compound 2 dielectric permittivity

| Number | Type      | Amplitude | Broadening | Center energy |
|--------|-----------|-----------|------------|---------------|
| 1      | Gaussian  | 2.410     | 0.206      | 1.957         |
| 2      | Gaussian  | 2.539     | 0.268      | 2.102         |
| 3      | Gaussian  | 1.268     | 0.323      | 2.269         |
| 4      | Gaussian  | 0.798     | 0.409      | 2.508         |
| 5      | Gaussian  | 0.569     | 0.499      | 3.338         |
| 6      | Gaussian  | 0.076     | 0.228      | 2.806         |

**Table S7.** Oscillator list for compound 3 dielectric permittivity

| Number | Type           | Amplitude | Broadening | Center energy |
|--------|----------------|-----------|------------|---------------|
| 1      | Gaussian       | 4.043     | 0.152      | 1.873         |
| 2      | Gaussian       | 4.632     | 0.274      | 2.028         |
| 3      | Gaussian       | 1.187     | 0.208      | 2.241         |
| 4      | Gaussian       | 0.655     | 0.339      | 2.488         |
| 5      | Gaussian       | 0.435     | 0.377      | 3.444         |
| 6      | Gaussian       | 0.268     | 0.417      | 2.662         |
| 7      | Tauc-Lorentz   | 1.237     | 21.157     | 0.482         |
### Table S8. Oscillator list for compound 4 dielectric permittivity

| Number | Type       | Amplitude | Broadening | Center energy |
|--------|------------|-----------|------------|---------------|
| 1      | Gaussian   | 4.653     | 0.093      | 1.746         |
| 2      | Gaussian   | 5.668     | 0.122      | 1.800         |
| 3      | Gaussian   | 4.751     | 0.204      | 1.915         |
| 4      | Gaussian   | 2.389     | 0.273      | 2.082         |
| 5      | Gaussian   | 0.515     | 0.223      | 2.311         |
| 6      | Gaussian   | 0.282     | 0.181      | 2.566         |
| 7      | Gaussian   | 0.306     | 0.252      | 2.715         |
| 8      | Gaussian   | 13.169    | 0.733      | 4.096         |
| 9      | Tauc-Lorentz | 32.099  | 0.088      | 1.690         |

### Table S9. Oscillator list for compound 5 dielectric permittivity

| Number | Type       | Amplitude | Broadening | Center energy |
|--------|------------|-----------|------------|---------------|
| 1      | Gaussian   | 4.670     | 0.093      | 1.726         |
| 2      | Gaussian   | 6.101     | 0.123      | 1.787         |
| 3      | Gaussian   | 5.068     | 0.243      | 1.911         |
| 4      | Gaussian   | 1.718     | 0.339      | 2.125         |
| 5      | Gaussian   | 0.338     | 0.259      | 2.626         |
Table S10. Oscillator list for in-plane compound 6 dielectric permittivity

| Number | Type      | Amplitude | Broadening | Center energy |
|--------|-----------|-----------|------------|---------------|
| 1      | Gaussian  | 1.316     | 0.122      | 1.695         |
| 2      | Gaussian  | 2.590     | 0.157      | 1.756         |
| 3      | Gaussian  | 3.467     | 0.260      | 1.859         |
| 4      | Gaussian  | 2.089     | 0.353      | 2.066         |
| 5      | Gaussian  | 1.150     | 0.323      | 2.570         |
| 6      | Gaussian  | 0.413     | 2.034      | 3.589         |
| 7      | Gaussian  | 47.977    | 0.025      | 0.024         |
| 9      | Tauc-Lorentz | 498.222 | 3.343      | 0.001         |

Table S11. Oscillator list for out-of-plane compound 6 dielectric permittivity

| Number | Type      | Amplitude | Broadening | Center energy |
|--------|-----------|-----------|------------|---------------|
| 1      | Gaussian  | 2.408     | 0.146      | 1.715         |
| 2      | Gaussian  | 3.008     | 0.160      | 1.755         |
| 3      | Gaussian  | 3.023     | 0.218      | 1.894         |
| 4      | Gaussian  | 2.175     | 0.277      | 2.027         |
| 5      | Gaussian  | 0.653     | 0.371      | 2.335         |
| 6      | Gaussian  | 0.365     | 0.460      | 2.587         |
| 7      | Gaussian  | 0.071     | 0.173      | 2.867         |
| 8      | Gaussian  | 0.390     | 0.567      | 3.158         |
| 9      | Tauc-Lorentz | 0.755 | 23.365     | 8.587         |
6. Reflection, transmission, absorption measurements and simulation data

**Figure S8** Measured data of six Curc series films (solid line) and simulated data (dashed line). Simulation data is obtained by use of dielectric permittivity spectrum of Figure 5.