

Ultra-Narrowband Near-Infrared Responsive J-Aggregates of Fused Quinoidal Tetracyanoindacenodithiophene

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Narrowband photoresponsive molecules are highly coveted in high-resolution imaging, sensing, and monochromatic photodetection, especially those extending into the near-infrared (NIR) spectral range. Here, a new class of J-aggregating materials based on quinoidal indacenodithiophenes (IDTs) that exhibit an ultra-narrowband (full width half maxima of 22 nm) NIR absorption peak centered at 770 nm is reported. The spectral width is readily tuned by the length of the solubilizing alkyl group, with longer chains resulting in significant spectral narrowing. The J-aggregate behavior is confirmed by a combination of excited state lifetime measurements and single-crystal X-ray diffraction measurements. Their utility as electron-transporting materials is demonstrated in both transistor and phototransistor devices, with the latter demonstrating good response at NIR wavelengths (780 nm) over a range of intensities.

1. Introduction

The J-aggregate is an important representative example of a supramolecular structure that is not only of pure academic interest, but also of relevance to applications in organic optoelectronics, due to its distinct optical and electronic properties.^[1] Self-assembled π -conjugated J-aggregates usually exhibit optical properties that differ strikingly from their corresponding monomers, with a significantly redshifted absorption in comparison to their monomeric species induced by the coupling of the transition dipole moments. In certain cases, this is also accompanied by an extreme sharpening of the redshifted absorption band caused

by exchange narrowing of the Frenkel excitons.^[2] They can also demonstrate interesting coherent, cooperative phenomena like superradiance.^[3]

Materials that absorb in the near-infrared (NIR) spectral range (i.e., beyond 750 nm) are of interest for many applications and an attractive approach to reach this NIR region is through the construction of supramolecular assemblies of organic materials that exhibit J-aggregation.^[4] To date, several molecular scaffolds have been reported to promote J-aggregates with assembly induced redshifted absorption. As shown in **Figure 1**, squaraine,^[5] cyanine,^[6] chlorophyll,^[7] perylene diimide (PDI),^[8] borondipyrromethene (BODIPY),^[9] hydroazaacene dicarboximide,^[10] and dibenz[a,j]anthracene-based macrocycle^[11] have opened up many opportunities for the design of narrowband NIR-responsive J-aggregates. Judicious molecular modifications have been employed to achieve the sharp, redshifted absorption and develop their respective structure-absorption relationships. These studies have demonstrated intermolecular interactions have a significant influence on formation of J-aggregates.^[12] For instance, squaraine and cationic cyanine dyes in water exploit either donor-acceptor interactions or hydrophobic effects to achieve the requisite slip-stacked molecular packing. Chlorophylls and PDI dyes use an interplay of multiple intermolecular forces, such as metal-ligand coordination, hydrogen bonding, and π - π interactions, to promote their J-aggregates.^[12b,13] Larger π -conjugated BODIPY, hydroazaacene dicarboximide, and macrocycle **1** rely on steric constraints to induce J-type couplings. Despite these developments, further classes of NIR-absorbing J-aggregates remain scarce and highly sought after.

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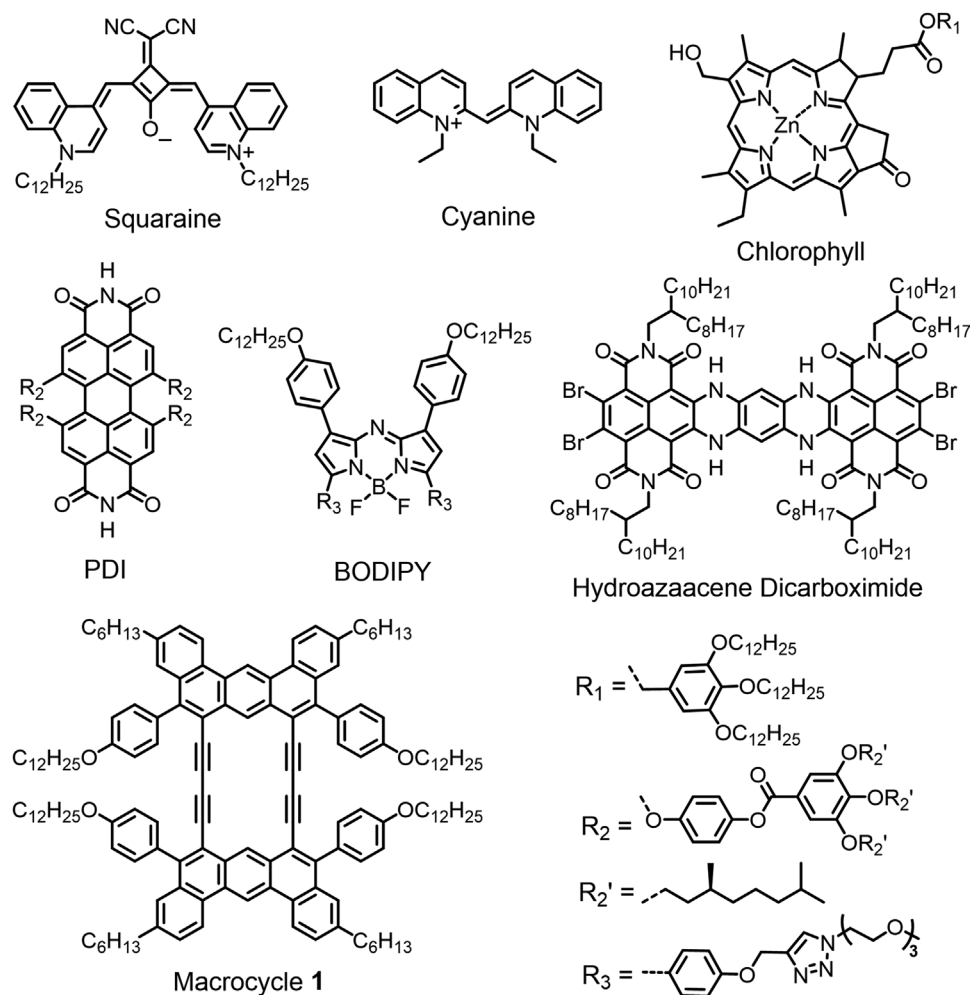


Figure 1. Representative molecular scaffolds for constructing narrowband NIR-absorbing J-aggregates.

NIR-responsive materials are highly attractive in a variety of technologies, such as organic photovoltaics (OPVs) and organic photodetectors (OPDs).^[14] In the OPV field, organic materials in the photoactive layer are required to possess a broadband or panchromatic absorption to the NIR region in order to harvest more photons. The development of NIR-absorbing materials has contributed greatly to boosting the efficiencies of single-junction OPVs, as well as enabling transparent and tandem OPV configurations.^[15] These broadband absorbing semiconductors have also been utilized in a range of panchromatic OPD applications such as imaging, optical communication, and diagnostics.^[16] However, narrowband photodetectors that are sensitive over a well-defined wavelength range, offer improved performance such as higher resolution for imaging or low light intensity detection.^[14c]

The utilization of narrowband absorbing material in OPDs is a straightforward approach for achieving monolithic band-selective photodetection. However, a limited number of NIR OPDs have been studied so far because of the scarcity of narrowband organic semiconductors in this spectral regime.^[17] In the absence of narrowband absorbers to obtain specific wavelength responses, device design strategies have been developed

using broadband absorbers combined with approaches such as optical filters and microcavity-induced narrowing, demonstrating spectral response widths of <100 nm.^[18] These device approaches generally require a thick active layer and inevitably increase the complexity of stacked imaging architectures. Therefore, it is highly desirable to prepare narrowband single-component OPDs with truly narrowband NIR-absorbing organic semiconductors.

In our search for near-IR absorbing n-type materials, we were interested in further exploring the potential of quinoidal compounds, which are known to show lower reorganization energy and smaller bandgaps compared with their aromatic analogues.^[19] Typically the oxidized, quinoidal structure is stabilized via the introduction of strongly electron-withdrawing endgroups, with the resulting materials exhibiting high electron affinity. As such they have demonstrated promising performance as n-type materials in organic thin-film transistors^[20] and organic solar cells devices,^[21] although they have not been widely investigated in OPDs.

We targeted the development of quinoidal materials containing the indacenodithiophene (IDT) core, a pentacyclic ladder-type arene of C_{2h} symmetry, which is widely applied

in constructing high-performance organic semiconductors in OPVs and organic transistors.^[22] The fused core IDT contains two bridging methylene units, which serve as convenient points for the attachment of solubilizing groups, which we hypothesized could be utilized to tune the solid state ordering of the resultant quinone. We hereby report three new quinoidal small molecules containing an electron-rich fused IDT core, together with electron accepting dicyanomethylene endgroups, named QIDT-C2C6, QIDT-C8, and QIDT-C16. By varying the length and branching point of the solubilizing alkyl side chains, the full-width at half-maximum (fwhm) of the absorption peak in the film state was impressively reduced in the following order: QIDT-C2C6 (142 nm) > QIDT-C8 (72 nm) > QIDT-C16 (22 nm). Interestingly, their absorption spectra in the solution state were identical and exhibited maximum absorption wavelengths (λ_{max}) at ≈ 650 nm with a shoulder peak at ≈ 695 nm. This striking difference in the film absorptions is attributed to J-aggregate formation, confirmed by a combination of single-crystal analysis and excited state lifetime measurements. Furthermore, the spectral responses of these materials were probed in a phototransistor configuration. Our results demonstrate

that this structurally simple quinoidal scaffold provides a new platform to construct ultra-narrowband NIR-responsive J-aggregates for wavelength-selective photodetection.

2. Results and Discussion

The QIDTs (with 2-ethylhexyl (C2C6), octyl (C8) and hexadecyl (C16) side chains) were obtained by a simple one-step Takahashi coupling reaction of respective dibrominated IDT and malononitrile in 55–65% yields (Figure 2a; Scheme S1, Supporting Information).^[23] All materials were readily isolated as crystalline powders after chromatographic purification and recrystallization. Interestingly each powder exhibited a distinctly different color (Figure 2b), from light green to dark green to brown. The chemical structures of QIDTs were confirmed by a combination of NMR (^1H and ^{13}C), variable-temperature ^1H NMR, MALDI-ToF mass spectrometry, elemental analysis, and single-crystal X-ray diffraction.

The electron accepting behavior of all materials was confirmed by cyclic voltammetry (CV). Comparable electrochemical

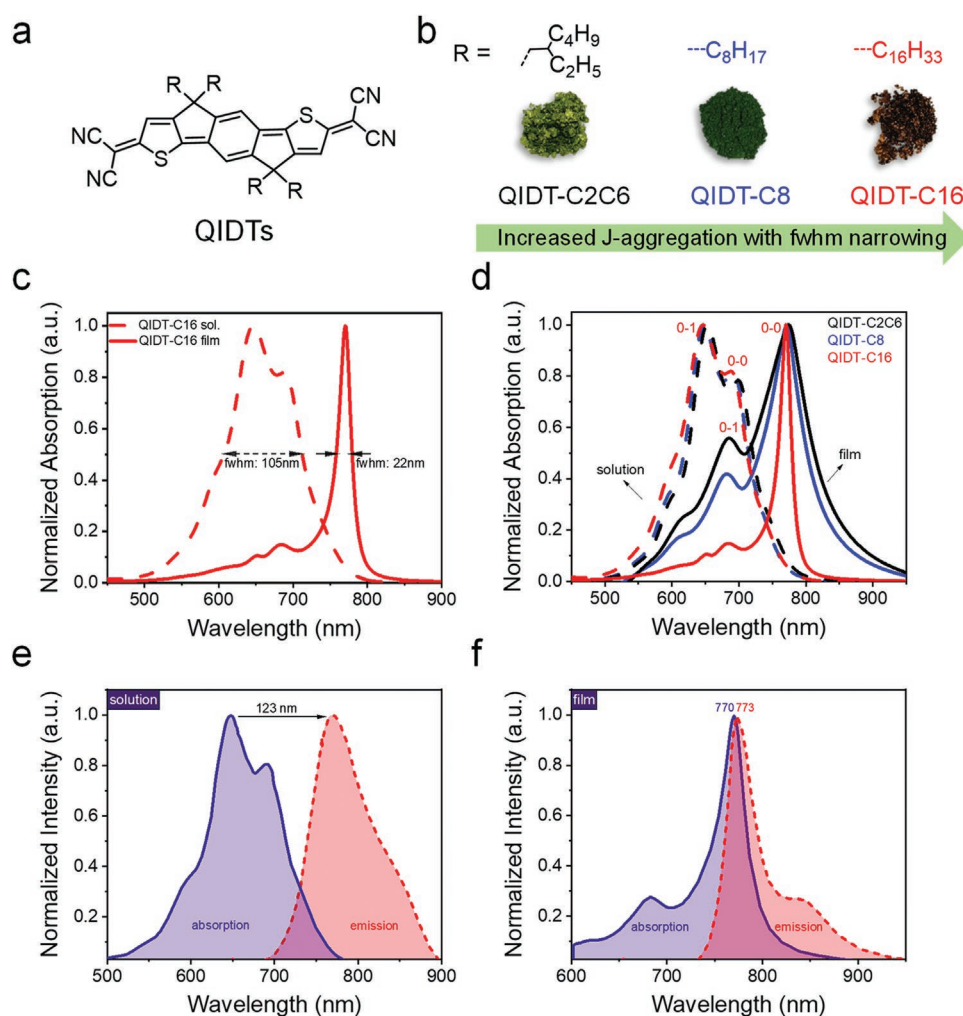


Figure 2. a) Chemical structures, b) visual appearance in solids, c,d) and absorption spectra of QIDTs in chloroform and spun-cast film (2 mg mL⁻¹ at 2000 rpm). e,f) Comparative UV-vis absorption and photoluminescence emission spectra in chloroform (e) and thin film (f) of QIDT-C16.

responses were observed in the solution state CV of all three QIDT materials collected in 0.1 M $[n\text{-Bu}_4\text{N}]\text{PF}_6$ /dichloroethane electrolyte, with all three materials undergoing reversible oxidation at 0.8 V versus Fc/Fc^+ (HOMO = -5.6 eV, Figure S4, Supporting Information). Both QIDT-C8 and QIDT-C2C6 also underwent two successive reversible reduction processes at -0.6 and -0.8 V, whereas only one reversible reduction at -0.6 V was observed for QIDT-C16. The slight difference in reduction behavior, despite their equivalent conjugated backbones, alludes to differing solution aggregation of QIDT-C16 as compared against QIDT-C8 and QIDT-C2C6.

All QIDT compounds exhibited good thermal stability, with 5 wt% loss occurring over 330 °C by thermogravimetric analysis (TGA, Figure S1, Supporting Information). They also exhibited excellent stability on storage in the ambient environment for over 1 year as powders, as demonstrated by ^1H NMR spectroscopy of fresh solutions. However, their solutions tended to degrade over a few days under ambient storage. The phase behavior, as investigated by differential scanning calorimetry (DSC) was complex and demonstrated clear differences dependent on sidechain. QIDT-C2C6 exhibited a sharp endotherm on melting at 182 °C, with a corresponding crystallization exotherm at 150 °C, with identical transitions seen on the second cycle. Changing to a linear octyl chain increased the melt temperature, with the initial cycle melting at 218 °C and subsequent cycles showing a reproducible crystalline melting up to 207 °C. The behavior of QIDT-C16 was more complex. Initial measurements cycling to 280 °C (as for the shorter analogues), resulted in a loss of any observable transitions, suggestive of some decomposition, despite the TGA data (Figure S1, Supporting Information). However, lowering the maximum temperature to 180 °C resulted in thermally reproducible behavior (Figure S3, Supporting Information). As well as a melt/crystallization at 156/149 °C, an additional exotherm was observed at 51 °C on cooling, together with two endotherms at 76 and 114 °C on heating. No evidence of liquid crystallinity was observed under cross-polarized optical microscopy, suggesting these are associated with crystal-crystal transitions.

The optical properties at room temperature ($\approx 25^\circ\text{C}$) were investigated by UV-vis absorption spectroscopy in dilute chloroform (CF) solution and as spun-cast thin films, as shown in Figure 2c,d, with the related data summarized in Table S1 (Supporting Information). In CF, all compounds showed well-structured absorption spectra along with high molar extinction coefficients of $1.12\text{--}1.36 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, which can be attributed to the rigid and planar nature of the quinoidal structure. The absorption spectra of the three quinoidal compounds in solution were almost identical, indicating that neither the length nor branching of the sidechain had any effect on the electronic structures of the molecules. Changing the solvent polarity from CF to chlorobenzene (CB), trichloroethylene (TCE), tetrahydrofuran (THF), toluene and cyclohexane (CYH), and methylcyclohexane (MCH) resulted in changes in the ratio of the 0–0 and 0–1 peaks together with a small blueshift of the absorption peaks as the solvent polarity decreased (Figure S7, Supporting Information). Dimerization in solution into an H-like geometry could be perhaps occurring, similar to that observed with pseudocyanine chloride aggregates, which showed dimer-like H-aggregate in solution but J-aggregate structure in the solid

phase.^[24] We note the absence of any significant changes in the spectra upon heating though, except for minor effects due to differences in refractive index as the solvent density changes (Figure S6, Supporting Information).

In comparison to the solution spectra, significant differences were apparent in the thin-film phase. First, the maximum absorption peaks of QIDTs in film were significantly bathochromic shifted by 123 nm to 770 nm, which suggested the existence of the J-aggregates. More dramatically, the absorption peaks dramatically sharpened and narrowed moving from C2C6 to C8 to C16, with QIDT-C16 exhibiting the classic ultrasharp peak indicative of J-aggregate exchange narrowing (FWHM = 142 nm for QIDT-C2C6, 72 nm for QIDT-C8, and 22 nm for QIDT-C16). The conjointly increased ratio of the film absorption intensities of the 0–0 and 0–1 bands was another reliable evidence for a classic J-aggregate.^[25] These results clearly indicate that the nature of the alkyl chain can strongly influence the extent of molecular aggregation and electronic coupling. It is also worth highlighting that this phenomenon is not limited to chloroform, but films processed from different solvents such as CB, toluene, TCE, THF, CYH, and MCH also exhibit similar J-aggregation with the same maximum peak position (Figure S5, Supporting Information). We note that the latter two solvents are marginal solvents for QIDT-16, whereas it exhibits excellent solubility in the former. The solvent choice does influence the FWHM; however, which reduces from TCE to toluene.

To further prove the presence of J-aggregates we studied the emission properties of the QIDTs in solution and thin film. A significant Stokes shift of ≈ 120 nm was observed in CF solution, with a smaller shift observed in non-polar solvents like using MCH or CYH (Figure 2e; Figure S10, Supporting Information). The quantum yields (ϕ) of fluorescence in solution, measured with respect to a near-IR standard, were low, 0.28–0.33% (Figure S14 and Table S2, Supporting Information), likely because of competing non-radiative processes due to the relatively long emission wavelength.^[26] Measurements of the film photoluminescence (PL) using a conventional fluorimeter (Figure S11, Supporting Information), resulted in a substantial dip in the emission spectra related to self-absorption effects due to the strong overlap between absorption and emission peaks (Figure S12, Supporting Information). The position of this dip was exactly at the absorption maximum (≈ 770 nm), and made accurate measurement of peak position difficult. Therefore, we utilized resonant Raman spectroscopy with laser excitation (514 nm), where we minimize the absorption and probe the emission extracted from fluorescence background in the Raman spectra selectively through resonant electronic excitation,^[27] as shown in Figure 2f. The emission spectrum of QIDT-C16 was a near mirror image of its absorption and with a very small Stokes shift of just 3 nm. Small Stokes shifts were also observed for the QIDT-C8 (7 nm) and QIDT-C2C6 (20 nm) thin films (Figure S12b, Supporting Information). QIDT-C16 with a narrow fluorescence band exhibited a stronger molecular delocalization. The sharp absorption in thin films and the small Stokes shift clearly suggested the presence of J-aggregates.

As an aside, we also investigated whether we could form the J-aggregate in solution, by the addition of a poor solvent to chloroform solutions. The addition of increasing aliquots

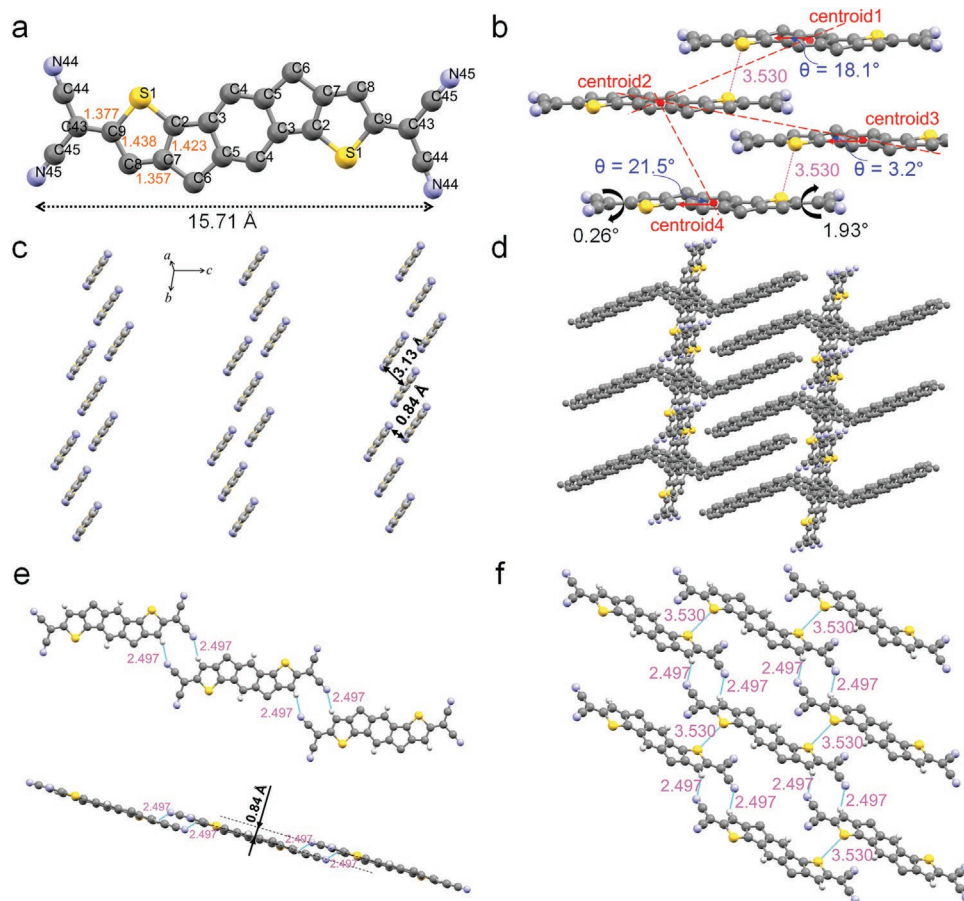


Figure 3. Single-crystal structure of QIDT-C16 in ball-and-stick model. Thermal ellipsoids are shown at 50% probability. a) Top view of QIDT-C16 and the molecular length of 15.71 Å, alkyl chains and hydrogen atoms are omitted for clarity. b,c) Molecular packing arrangement of QIDT-C16 with stacking distances of 0.84 and 3.13 Å between molecular planes, with slipping angles of 3.2° and 18.1°. d) The interdigitation of the $C_{16}H_{33}$ alkyl chains of adjacent sheets. e) Top-down and side-on views of intramolecular short contacts. f) Extended slipped stacking.

of either octane or methanol, as non-polar and polar poor solvents, respectively, was investigated. Addition of octane resulted in a hypsochromic absorption shift, while the more polar methanol resulting in a bathochromic absorption shift. Their changing spectral trend was reflected by the corresponding PL spectra (Figures S8 and S9, Supporting Information). However, apart from the solvachromic effects, we were not able to observe J-aggregate formation in solution under these conditions.

Single-crystal structure analysis has been applied for decisive identification of the quinoidal QIDTs and their molecular packing motifs. Single crystals of QIDTs were obtained from a CF/MeOH solvent mixture by slow solvent evaporation. The diffraction-derived single-crystal structure of QIDT-16, as the representative of this QIDT family, is shown in **Figure 3** and Figure S19 (Supporting Information), and detailed crystal structure data are summarized in Supporting Information. As shown in Figure 3a, the molecular length of QIDT-C16 is 15.71 Å. The bond lengths of C7–C8 and C9–C43 are shorter than that of a typical $C(sp^2)$ – $C(sp^2)$ single bond (≈ 1.45 Å) but are close to the length of a typical $C(sp^2)$ – $C(sp^2)$ double bond (≈ 1.34 Å). Meanwhile, the bond lengths of C2–C7 and C8–C9 are longer than that of a typical $C(sp^2)$ – $C(sp^2)$ double bond.

This alternation in bond lengths clearly confirms the quinoidal framework of these QIDT compounds.^[28]

Figure 3b shows that QIDT-C16 recrystallizes in the triclinic space group of P-1. The QIDT-C16 main core and the two end-capped cyano groups are close to coplanar, showing small torsional angles of 0.26–1.93°. The QIDT-C16 is organized parallelly in a slip-stacked arrangement with slip angles of $\theta < 3.2^\circ$ and 18.1° , which is unequivocally regarded as a J-aggregate. Along the slip stack $CN \cdots H$ contacts (2.49 Å) between the β -H of the thienyl ring and the nitrile of an adjacent molecule exist, similar to those observed in other quinoids.^[29] Adjacent stacks show short $S \cdots S$ contacts of 3.53 Å, suggestive of intramolecular non-bonding interactions. The QIDT-C16 possesses brick-type stack molecular packing arrangement and the short main-core stacking distances of closely packed core are 0.84 and 3.13 Å (Figure 3c; Supporting Information). Note the values are the distances between two adjacent molecular planes, not a “face-to-face” stacking distance. The $C_{16}H_{33}$ alkyl chains of adjacent sheets interdigitate to form lamella-like structures, as shown in Figure 3d. In comparison, QIDT-C8 crystallized in the same space group, but with subtle differences in crystal packing compared to QIDT-C16. Thus, intramolecular $CN \cdots H$ contacts between molecules in slipped stacks increased to

2.74 Å, and the S...S distance to 3.69 Å, and the slip angles θ changed to 5.1° and 11.5°.

In the case of QIDT-C2C6, the mixture of stereoisomers induced by the ethylhexyl chains leads to significant disorder (see Supporting Information),^[21a] with the volume they occupy in the crystal resembling a highly diffused smear of electron density rather than having discrete electron density peaks. So, the various partial occupancy orientations that were modeled are, by necessity, poor approximations of the likely reality and so should be treated with caution. Nevertheless, the crystallographic analysis of the aromatic cores of QIDT-C2C6 is reliable and confirms the chemical structure. The QIDT-C2C6 structure crystallized with two independent molecules (QIDT-C2C6-A and QIDT-C2C6-B) in the asymmetric unit, shown in Figure S17 (Supporting Information).

Femtosecond transient absorption spectroscopy (fs-TAS) was performed to investigate the effect of J-aggregate behavior on charge carrier dynamics in the three QIDT films. The transient absorption spectra of three QIDT films are shown in Figure S22 (Supporting Information). At early time delays (<1 ps), negative ground state bleaching (GSB) signals are visible at 780 nm, and positive photoinduced absorption observed at 918 nm, both assigned to photogenerated excitons. The exciton photoinduced absorption signal at 918 nm exhibits a rapid (ps) decay, correlated with the rise of an absorption signal at 500 nm (Figure 4). These ps dynamics, which are fluence independent (see data for QIDT-C16 in Figure S24, Supporting Information) are assigned to a monomolecular exciton relaxation processes within the manifold of exciton states. It is apparent that this exciton relaxation process is fastest with QIDT-C16 (0.25 ps) compared to QIDT-C2C6 (5.6 ps) and QIDT-C8 (3.4 ps) with branched and shorter side chains. This trend in exciton relaxation dynamics indicates J-aggregates of QIDT-C16 exhibiting the strongest intermolecular interactions and exciton effects, consistent with the steady state spectroscopic and crystallographic data above.^[30]

Finally, the strong laser-like absorption of QIDT-C16 in the NIR spectrum range motivated us to study the application

of QIDT-based organic transistors and phototransistors as NIR light sensors. The charge transport properties of QIDTs were initially characterized using thin-film transistor (TFTs) measurements. Bottom-gate, bottom-contact (BGBC) TFTs were fabricated on octadecyltrichlorosilane (OTS)-modified SiO₂ (400 nm)/Si substrates. Thin films were spin-coated as the organic semiconducting layer (≈ 40 nm), and 40 nm gold served as the source and drain electrodes. The ensuing TFTs show electron mobility of 3.7×10^{-3} to ≈ 0.023 cm² V⁻¹ s⁻¹ depending on the sidechain length, with QIDT-C16 exhibiting the highest performance (Figure S25 and Table S6, Supporting Information). Attempts to improve performance by thermal annealing or blending with the inert binder poly(α -methyl styrene) (PaMS), which has previously been reported as a route to improve performance,^[20a] were unsuccessful. No significant changes were observed in our case, which we attribute to the large crystalline aggregates in the films (Figure S26, Supporting Information). Despite this, the transfer and output characteristics showed negligible hysteresis between forward and reverse sweeps, indicating low trap density levels for electron transport.

Phototransistors were fabricated in order to further explore the potential for photodetection application of these NIR J-aggregates. Surprisingly, there have been limited reports on the use of n-type materials in phototransistors,^[31] despite their importance to develop logic circuits.^[32] TFTs were prepared via a scalable blade coating technique (channel length (*L*): 40 μ m; channel width (*W*): 1000 μ m), and they were tested in dark and under illumination using a NIR light-emitting diode, with an emission wavelength centered at ≈ 780 nm, at a constant optical power density of ≈ 270 W cm⁻². The field-effect transistor and phototransistor performances of C16, C2C6, and C8 are shown in the Figure 5, Figures S27 and S28 (Supporting Information), respectively. Figure 5a displays the transfer curves for the linear and saturation region in the dark and the square root of the saturation current versus gate voltage (*V*_G) curve. Figure 5b includes the output curves and Figure 5c depicts the comparison of transfer characteristics for the saturation

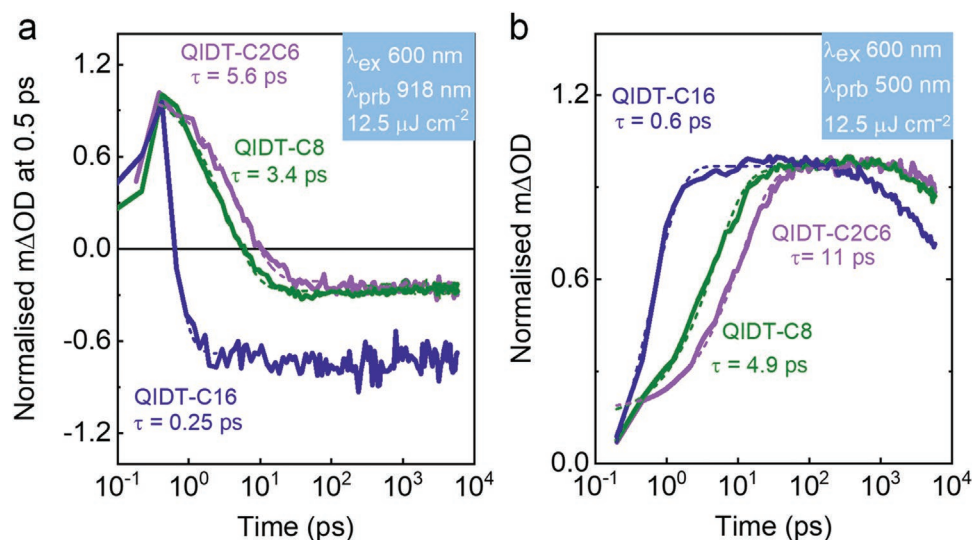


Figure 4. a,b) Transient absorption decay dynamics for QIDT films, excited at 600 nm and probed at 918 nm (a) and 500 nm (b). The dashed lines are fits to a single exponential decay and growth, respectively.

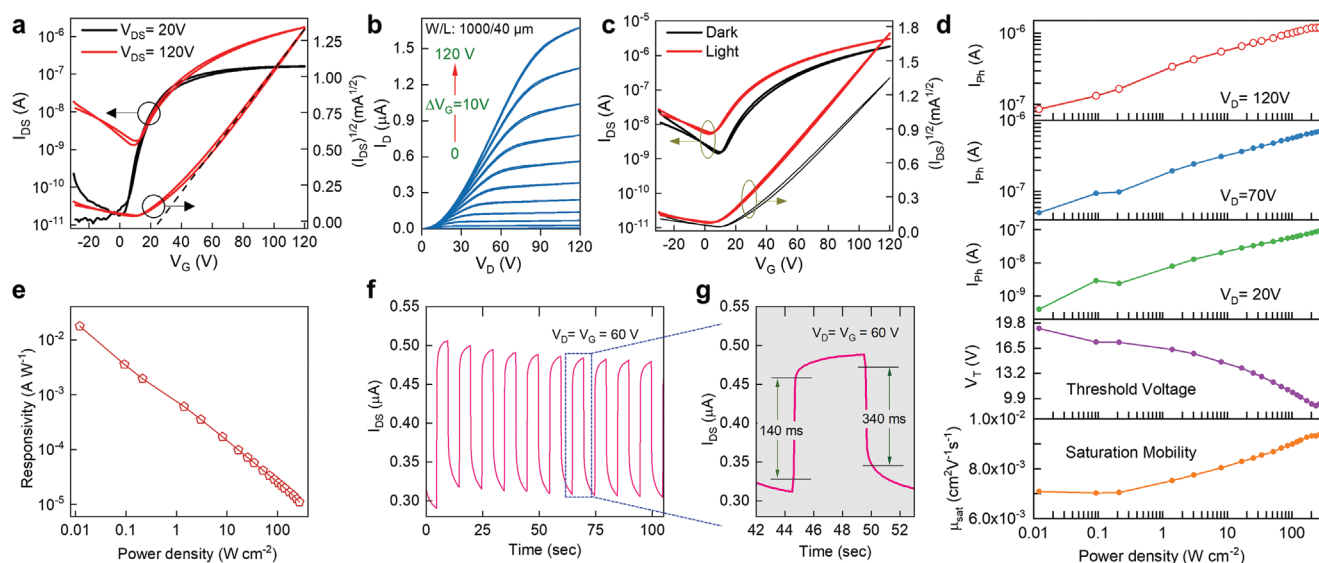


Figure 5. Organic thin-film phototransistor characterization of QIDT-C16. a) Transfer characteristics in the linear and saturation region, b) output characteristics, c) comparison of the transfer curves in the absence and presence of light (780 nm; 108 mW), d) light sensitivity analysis using different device parameters, e) the responsivity and detectivity, f) light chopping measurement at 780 nm wavelength and 108 mW intensity, and g) expanded image of one of the optical responses for rise and fall time determination.

region in the dark and under illumination. The figure shows substantial improvement in device parameters such as photocurrent ($I_{Ph} = I_{illumination} - I_{dark}$) and threshold voltage (V_{Th}) under illumination. I_{Ph} and V_{Th} along with the saturation field-effect mobility (μ_{sat}) are further quantitatively measured with increasing power density of the incident light (Figure 5d). In comparison with C2C6 (Figure S28d, Supporting Information) and C8 (Figure S29d, Supporting Information), all the different device parameters are improved steadily with increasing illumination. However, the C2C6 and C8 devices lack consistency in phototransistor performance. The μ_{sat} for these devices gradually dropped with increasing optical power density and the linear and saturation photocurrents saturate after $\approx 20 \text{ W cm}^{-2}$.

Responsivity of the devices were calculated using the following equation:

$$R = \frac{I_{light} - I_{dark}}{P_{in}} \quad (1)$$

where I_{light} and I_{dark} are the device current at illumination and dark, respectively, P_{in} is the power of the incident light. Figure 5e, Figures S27e and S28e (Supporting Information) represent the change in responsivity with the power density at 120 V drain voltage (V_D) and V_G . The maximum responsivity (R_{max}) of QIDT-C16 devices was found to be slightly better than the other two molecules.

For detectivity calculation, we use the following equation where we assume the dark current is dominated by the shot noise.^[33]

$$D^* = \frac{R\sqrt{A}}{\sqrt{2eI_{dark}}} \quad (2)$$

Here, A is the active area of the phototransistor, and e is the electron charge. Generally, the OFETs with lower W/L greatly

suffers from the fringe effect where the peripheral channels contribute to the channel width and length.^[34] As the W/L of the devices used in the measurements are considerably high ($W/L = 25$), we neglected the contribution of the peripheral channel and calculated the active area as a product of W and L . The D^* values for all the devices at 0.01 W cm^{-2} power density can be found in Table S7 (Supporting Information). The light chopping data at 1375 W cm^{-2} illumination power density is represented in the Figure 5f, and one of the optical responses is expanded in Figure 5g. The rise and fall time are measured to be 140 and 430 ms, respectively. In order to observe the photoreponse of the device for small illumination intensity variations, the change in drain current (I_D) at a constant V_D and V_G with increasing illumination intensities is measured (Figure S30, Supporting Information), where we found the QIDT-C16 device is photoresponsive throughout the intensity range. The photo response data for the QIDTs blade coated devices are summarized in Table S7 (Supporting Information). Although the TFT performance of QIDT-C16 devices are slightly lower than QIDT-C2C6 and QIDT-C8 devices, the phototransistor properties are better compared to these devices and also showed consistent photoreponse throughout the illumination intensity range at 780 nm wavelength.

3. Conclusion

We have developed three new fused tetracyanoindacenodithiophene quinoids (i.e., QIDTs) that exhibit striking differences between their solution and thin-film UV-vis absorptions. Upon film formation, the QIDTs showed redshifted absorption, changed spectral profiles, narrowed bandwidths, and small Stokes shifts consistent with the formation J-aggregates. The sharpness of the J-aggregate peak could be readily tuned by altering the sidechain length on the QIDT, with the C16

derivative exhibiting an ultranarrow peak (FWHM of 22 nm) with minimal absorption in the visible region. Single-crystal X-ray analysis suggest that the differences are due to subtle changes in the slip-stacked packing arrangement caused by the sidechain length. Pump-probe transient absorption spectroscopy measurements demonstrate that QIDT-C16, with the sharpest J-aggregate peak, exhibited the most rapid exciton decay, consistent with J-aggregate formation. Finally, NIR phototransistors were fabricated showing consistent photoresponse throughout the illumination intensity range at 780 nm wavelength. Our results highlight that sidechain tuning is a valuable strategy for optimizing J-aggregate behavior in the previously unreported class of quinoidal indacenodithiophene acceptors.

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

indacenodithiophenes, J-aggregates, narrow absorption, organic semiconductors, quinoidal materials

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