Accepted Manuscript

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PII: S0143-7208(15)00237-5

DOI: [10.1016/j.dyepig.2015.06.019](https://doi.org/10.1016/j.dyepig.2015.06.019)

Reference: DYPI 4821

To appear in: *Dyes and Pigments*

Received Date: 18 May 2015

Revised Date: 8 June 2015

Accepted Date: 10 June 2015

Please cite this article as: Qi Q, Li R, Luo J, Zheng B, Huang K-W, Wang P, Wu J, Push-Pull Type Porphyrin Based Sensitizers: The Effect of Donor Structure on the Light-Harvesting Ability and Photovoltaic Performance, *Dyes and Pigments* (2015), doi: 10.1016/j.dyepig.2015.06.019.

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Graphical Abstract:

Replacing one phenyl ring in the triphenylamine donor moiety by an anthryl unit in the push-pull porphyrin based sensitizers significantly improved the light harvesting capability and power conversion efficiency.

Push-Pull Type Porphyrin Based Sensitizers: the Effect of Donor Structure on the Light-Harvesting Ability and Photovoltaic Performance

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ABSTRACT: Push-pull type porphyrin-based sensitizers have become promising candidates for high-efficiency dye sensitized solar cells (DSCs). It is of importance to understand the fundamental structure-physical property-photovoltaic performance relationships by varying the donor and acceptor moieties. In this work, two new porphyrin-based sensitizers, WW-7 and WW-8, were synthesized and compared with the known sensitizer YD20. All the three dyes have the same porphyrin core and acceptor group (ethynylbenzoic acid) but their donor groups vary from the triphenylamine in YD20 to *meso*- diphenylaminoanthracene in WW-7 to *N*-phenyl carbazole in WW-8. Co(II/III)-based DSC device characterizations revealed that WW-7 showed enhanced light harvesting ability in comparison to YD20 with improved incident photon-to-collected electron conversion efficiencies (IPCEs). As a result, WW-7 displayed much higher short circuit current (J_{sc} : 13.54 mA cm⁻²) and open-circuit voltage (V_{oc} : 0.829 V), with a power conversion efficiency (η) as high as 7.7%. Under the same conditions, YD20 cell exhibited a power conversion efficiency of 6.6% and the dye WW-8 showed even lower efficiency (η = 4.6%). Detailed physical measurements and theoretic calculations were conducted to understand the difference and reveal how three different donor structures affect their molecular orbital profile, light-harvesting ability, energy level alignment, and eventually the photovoltaic performance.

KEYWORDS: Push-pull, porphyrin, anthracene, carbazole, solar cell.

Dye-sensitized solar cells (DSCs) have drawn a rising interest due to the low production cost, good conversion efficiency, ease of fabrication and environmental concerns [1]. Design and synthesis of stable organic dyes with appropriate push-pull structure was proved to be the key to achieve highly efficient DSCs. Based on this principle, various types of organic dyes with donor- π -acceptor (D- π -A) system have been investigated [2]. Among these dyes, push-pull type porphyrin-based sensitizers are considered to be promising candidates for DSCs because of the facile functionality and their excellent light-harvesting properties [3]. In 2011, a zinc porphyrin sensitizer (YD2-*o*-C8) co-sensitized with an organic dye (Y123) using a cobalt-based electrolyte attained a power conversion efficiency (η) of 12.3%, which is superior to those developed based on Ru complexes [4]. Recently, the performance of porphyrin-based sensitizers is improved even higher [5].

For further improvement of the device, it is however highly desirable to develop new dyes with even enhanced light harvesting ability both in the visible (ca. 400-700nm) and the near infrared (NIR) region (ca. 700-1400 nm) since a significant portion of solar energy falls within this range [6]. Extending the π -conjugation of a sensitizer is a logical and most common way to achieve such a goal. Based on the structure of YD2-*o*-C8, many strategies were applied to design and synthesize porphyrin-based sensitizers with extended π -conjugation in order to enhance the light-harvesting ability [7]. Among these attempts, phenylethynyl (PE) group was widely used as π -spacer in the design of porphyrin-based sensitizers in order to extend the π -conjugation and to form a well-defined and rigid structural arrangement [8]. In addition, the choice of donor is critical to achieve good light-harvesting ability and efficient intramolecular charge separation upon photo-irradiation. So far, one of the most often used donors in organic sensitizers is triphenylamine. For example, the porphyrin-based dye YD20 (Fig. 1) gave high power conversion efficiency (η : 8.1%) as reported by Yeh and Diau *et al* [8e]. How to further improve the performance is critical and we expect the following modifications on the donor structure could work: (1) replacing the phenyl spacer by a more π -extended anthracene unit will enhance the light-harvesting ability (i.e., “benzannulation” approach, Fig. 1); (2) replacing the diphenylamino unit with a carbazole group could lower down the HOMO energy level and thus enhance dye generation driving force [9a] (i.e., “ring fusion” approach, Fig. 1). So far, the donor moiety of many porphyrin-based sensitizers is mainly limited to diphenylamino groups, and examples of modification with *N*-fused heterocycles are few [9]. Based on these considerations, in this work two new porphyrin dyes, WW-7 and WW-8 were synthesized and compared with the dye YD20 (Fig. 1).

2. Experimental section

2.1. Materials and instruments

All reagents and starting materials were obtained from commercial suppliers and used without further purification unless otherwise noted. Anhydrous toluene and THF were distilled from sodium-benzophenone immediately prior to use. The ^1H NMR and ^{13}C NMR spectra were recorded in solution of CDCl_3 or THF-d_8 on Bruker DPX 300 or DRX 500 NMR spectrometers with tetramethylsilane (TMS) as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d

= doublet, t = triplet, m = multiplet. MALDI-TOF or APCI mass spectrometry was used to confirm the mass of compound. The electrochemical measurements were carried out in anhydrous methylene chloride with 0.1 M TBAPF₆ as the supporting electrolyte at room temperature under the protection of nitrogen. A gold stick was used as working electrode, platinum wire was used as counting electrode, and Ag/AgCl (3M KCl solution) was used as reference electrode. The potential was externally calibrated against the ferrocene/ferrocenium couple. Steady-state UV-vis absorption were recorded on a Shimadzu UV-1700 spectrometer. The solvents used for UV-vis measurements are of HPLC grade (Merck). The synthetic details of WW-7 and WW-8 are described in the Electronic Supplementary Information.

2.2. DSC Fabrication and Characterization

A 4.2- μ m-thick, transparent layer of 25-nm-sized TiO₂ particles was first screen-printed on FTO glass (Nippon Sheet Glass, Solar, 4 mm thick) and further coated with a 5.0- μ m-thick second layer of scattering titania particles (WER4-O, Dyesol) to produce a bilayer titania film, which was used later as the negative electrode of a DSC. The preparation procedures of TiO₂ nanocrystals and paste for screen-printing were reported in a previous paper [10]. The film thickness was monitored with a bench-top Ambios XP-1 stylus profilometer. After sintering at 500 °C and cooling to 80 °C, a circular titania electrode (~ 0.28 cm²) was stained by immersing it overnight into a solution of 150 μ M dye dissolved in a binary solvent of THF and ethanol (volume ratio, 1/4). The dye-coated titania electrode was then rinsed with acetonitrile and dried by air flow, and was further assembled with a thermally platinized FTO positive electrode by a 25-mm-thick Surlyn (DuPont) hot-melt gasket and sealed up by heating. The internal space was perfused with an electrolyte with the aid of a vacuum-back-filling system.

Transient photoelectrical experiments were measured with an Autolab-PGSTAT302N electrochemical workstation. The steady and perturbing lights on the photoanode side of a testing cell were supplied with white and red light-emitting diodes, respectively. We used the red light to generate a photovoltage perturbation near the open-circuit photovoltage of a testing cell under a certain white light and measured the voltage decay process thereafter. The modulated photovoltage by the red pulse of a testing cell was below 5 mV. The electron lifetime can be obtained by fitting a stretched exponential function to the photovoltage decay. The electron density was estimated by the charge extraction method. A testing cell was first kept at open circuit under white light and subsequently the white light was turned off upon switching the cell from open circuit to short circuit to record the resulting current transient, and the electron density was obtained by current integration.

3. Results and discussion

3.1. Synthesis of materials.

The synthetic route for the porphyrin dyes WW-7 and WW-8 is outlined in Scheme 1. The reference porphyrin dye YD-20,²¹ and the intermediate compounds **1** [11], **4** [4] and **5** [12] were synthesized as previously reported. Compound **2** was synthesized in 98% yield by bromination of **1** with *N*-bromosuccinimide (NBS) catalyzed by FeCl₃ [13]. Sonogashira coupling of **2** with trimethylsilylacetylene followed

by desilylation with K_2CO_3 gave the terminal alkyne **3**. Porphyrin dyes WW-7 and WW-8 were then synthesized in 40-50% yields via Sonogashira coupling between **3** or **5** with intermediate **4**, followed by desilylation with tetrabutylammonium fluoride (TABF), and another Sonogashira coupling reaction with 4-iodobenzoic acid. The dyes WW-7 and WW-8 are green solid and soluble in normal solvents such as dichloromethane (DCM), chloroform and tetrahydrofuran (THF). They were thoroughly characterized by 1H NMR, ^{13}C NMR, and high resolution mass spectrometry (HR MS) (ESI $^+$).

3.2. Optical properties

The absorption spectra of WW7, WW8 and YD20 in chloroform are shown in Fig. 2 and the data are collected in Table 1. All three dyes show an intense Soret absorption in the range 400-550 nm and a moderate Q band at 550-725 nm. Compared with YD20 (Soret band at 457 nm, $\epsilon = 221000\text{ M}^{-1}\text{cm}^{-1}$, and Q band at 667 nm, $\epsilon = 56000\text{ M}^{-1}\text{cm}^{-1}$), dye WW-7 exhibits much broader Soret band at 454 nm ($\epsilon = 186000\text{ M}^{-1}\text{cm}^{-1}$) and Q band at 664 nm ($\epsilon = 69000\text{ M}^{-1}\text{cm}^{-1}$), which is desirable for light harvesting, while dye WW-8 displays much more intensive Soret band at 451 nm ($\epsilon = 416000\text{ M}^{-1}\text{cm}^{-1}$) and slightly higher absorption coefficient at Q band (620 nm, $\epsilon = 64500\text{ M}^{-1}\text{cm}^{-1}$), but both bands are blue-shifted. Therefore, the introduction of an anthracene moiety has a dominant impact on broadening of the absorption spectrum and there is only slightly blue shift of the maxima of Soret and Q-band compared to YD20. The optical energy gaps (E_g^{opt}) of WW-7, WW-8 and YD20 were estimated from the absorption onset as 1.73, 1.86, 1.79 eV, respectively.

3.3. Electrochemical Properties

The electrochemical properties of WW-7, WW-8 and the reference YD20 were investigated by cyclic voltammetry (CV) in deoxygenated DCM solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF $_6$) as supporting electrolyte (Fig. 3). Multiple quasi-reversible or irreversible redox waves were observed for all four compounds (see the list of half wave potentials $E^{1/2}_{\text{ox}}$ (anodic scan) and $E^{1/2}_{\text{red}}$ (cathodic scan) in Table 1. The oxidations are corresponding to electron abstractions from both the amino functional group and the porphyrin ring [14a, 14b]. The first oxidation potential of WW-8 is less positive than these of WW-7 and YD20, indicating the electron-donating effect of the amino functional group containing anthracene. The reductions are corresponding to reduction of the anchoring group and/or the formation of a zinc porphyrin anion radical and di-anion [14b]. The HOMO and LUMO energy levels were estimated according to equations: $\text{HOMO} = -[4.8 + E_{\text{ox}}^{\text{onset}}]\text{ eV}$, and $\text{LUMO} = -[4.8 + E_{\text{red}}^{\text{onset}}]\text{ eV}$, where $E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$ are the onset of the first oxidation and reduction wave respectively (vs. Fc^+/Fc) [14c]. The HOMO and LUMO energy levels for WW-7, WW-8 and YD20 were determined to be -5.20, -5.24, -5.02 eV (HOMO) and -3.74, -3.36, -3.38 eV (LUMO), respectively. The corresponding electrochemical energy gaps (E_g^{EC}) were calculated to be 1.46, 1.78 and 1.64 eV, which are in agreement with the optical energy gap values. Thus, introduction of an anthracene unit in WW-7 significantly lowers both LUMO and the HOMO energy levels compared to the reference (YD20), leading to a narrowed

energy gap. However, replacement of the diphenylamino group in YD20 by a carbazole unit in WW-8 results in a decrease of HOMO and slight up-lift of LUMO, accompanied with a larger energy gap.

3.4. TD DFT calculations

In order to gain better understanding of the molecular geometries, molecular orbitals, optical properties, and electronic properties of the porphyrin dyes WW-7, WW-8 and YD20, TD DFT calculations at the B3LYP/6-31G** level of theory were performed. Fig. 4 shows their optimized molecular structures and frontier molecular orbital profiles together with the calculated energy levels of HOMOs and LUMOs. For WW-7, the HOMO is delocalized along both the donor moiety and porphyrin core, while the LUMO is delocalized through the porphyrin core and the acid binding group, similar to YD20. Such a disjoint character of HOMO and LUMO distribution allows a fast intramolecular charge transfer transition. WW-8 shows lower HOMO energy level compared with YD20, which could be good for achieving a higher V_{oc} value. However, the HOMO and LUMO are not well segregated, which means that intramolecular charge transfer may be less efficient compared with WW-7 and YD20. Time-dependent DFT calculations predicted that WW-7, WW-8 and YD20 show the longest-wavelength absorption onset at 980, 780 and 890 nm, respectively, together with a broad spectra (ESI[†]), and this trend is well in agreement with the experimental data.

3.5. Photovoltaic Properties

The newly synthesized dyes were adsorbed onto a bilayer (4.2+5.0 μm) titania film [15] by using an optimized binary solvent system of THF and ethanol (volume ration 1:4) to serve as a working electrode for photovoltaic characterizations. Our cobalt electrolyte is composed of 0.25 M tris(2,2'-bipyridine) cobalt(II) di[bis(trifluoromethanesulfonyl)imide], 0.05 M tris(2,2'-bipyridine)cobalt(III) tris[bis(trifluoromethanesulfonyl)imide], 0.5 M 4-*tert*-butylpyridine (TBP) and 0.1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in acetonitrile. The dye-loading density of WW-7, WW-8 and YD20 was measured as 1.18×10^{-8} , 1.62×10^{-8} and 0.96×10^{-8} mol cm^{-2} μm^{-1} , respectively. Fig. 5b shows the photocurrent action spectra for WW-7 and WW-8 cells measured under standard photovoltaic reporting conditions (global AM1.5 sunlight with irradiance of 100 mW cm^{-2} at 298 K), with YD20 as the reference cell. This is in good accordance with the electronic absorption of the 4.2 μm -thick, dye-grafted titania films (Fig. 5a). We also measure photocurrent density–voltage (j – V) characteristics at an irradiance of 100 mW cm^{-2} , simulated AM1.5 sunlight (Fig. 6a). The photovoltaic parameters are listed in Table 2.

When WW-7 was tested for the photovoltaic performance, it showed much better performance among the three dyes. Indeed, when WW-7 was employed, an impressive broad IPCE action spectrum covering the panchromatic visible region and part of the NIR region was achieved. The IPCE values (>50% from 410 nm to 730 nm) are comparable to that of YD20 under same conditions. The most distinct character is that the width of photocurrent action spectrum was further improved for WW-7 cell, as a result, a higher short-circuit current (J_{sc}) value of 13.54 mA cm^{-2} was achieved for WW-7 sensitized solar cells, in comparison to a J_{sc} of 12.93 mA cm^{-2} for YD20 cell. Moreover, the V_{oc} value of WW-7 cell (0.829 V) is much higher than that of the latter (0.774 V), and its fill factor (FF) is also slightly higher. As a result, the overall power conversion efficiency of the WW-7 cell reached

7.7%, which exceeds YD20 cell ($\eta = 6.6\%$) at the same testing condition. Unfortunately, WW-8 possessed a carbazole donor moiety showed only moderate power conversion efficiency of 4.6%, which can be mainly attributed to the low J_{sc} value (8.02 mA cm^{-1}). Dye WW-8 showed IPCE values exceeding 20% from 385 nm up to 700 nm, with a big gap at the middle, which is in consistence with its absorption spectrum. This moderate light harvesting ability limits the J_{sc} value and eventually the efficiency although it has the highest dye loading density. The lower V_{oc} value compared with YD20 could be originated to the less efficient electron injection from the photo-excited dyes to the conduction band of the TiO_2 and/or back electron transfer at the interfaces.

To further understand the dye structure-device performance relationship, we conducted further physical measurements on the WW-7 and the WW-8 cells with the YD20 cell as a reference. For a short-circuit DSC device, it is known that the J_{sc} is measured at the condition of a considerable low electron density in the nanocrystalline titania film and the charge recombination flux is significantly reduced. Thereby, the measured J_{sc} is roughly proportional to the photocarrier generation flux. The validity of this analysis motivated us to compare the dye structure correlated V_{oc} variation at a given J_{sc} by measuring J - V curves under various light intensities and plotting V_{oc} as a function of J_{sc} (Fig. 6b). It is noted that at a given J_{sc} , the WW-7 cell exhibits a higher V_{oc} than YD20, while WW-8 gives the lowest V_{oc} value.

It is widely recognized that for a fixed redox electrolyte in DSCs, the rise or fall of V_{oc} is determined by the titania electron quasi-Fermi-level ($E_{F,n}$), which intrinsically stems from a change of titania conduction band edge (E_c) and/or a variation of titania electron density [15,16]. At a given flux of photocarrier generation, the titania electron density is determined by the interfacial recombination rate of titania electrons with electron accepting species in electrolytes and/or dye cations. Thereby charge extraction (CE) and transient photovoltage decay (TPD) measurements [17] were further carried out to understand the electronic origins of the aforesaid V_{oc} fluctuation. As shown in Fig. 7a, the cells made with WW-7 and YD20 give a similar extracted charge (Q) at the same potential bias V_{oc} , suggesting a fixed conduction-band edge of titania with respect to the electrolyte Fermi-level, whereas the WW-8 cell exhibits a larger extracted charge (Q) at the same V_{oc} , suggesting a downward shift of titania conduction band edge (E_c) with respect to the electrolyte Femi level. And this may give evidence for lower V_{oc} of cell with WW-8. As Fig. 7b presents, the WW-7 cell displays much longer charge recombination lifetime (τ) than WW-8 and YD20 cells at a given charge Q , accounting for the aforementioned superior photovoltage at a given J_{sc} for WW-7, followed by WW-8.

4. Conclusions

In summary, we have synthesized two new porphyrin-based sensitizers WW-7 and WW-8 together with YD20 as reference. Improved optical, electrochemical and photovoltaic properties were achieved by applying diphenylamino and anthryl groups as donors. Co(II/III)-based DSC device characterizations showed that WW-7 displayed better J_{sc} (13.54 mA cm^{-2}), V_{oc} (0.829 V) and power conversion efficiency ($\eta = 7.7\%$) than YD20. However, WW-8 with *N*-fused carbazole as donor exhibited only moderate performance ($\eta = 4.6\%$) mainly due to its low light harvesting capability and less efficient intramolecular charge separation. Our results implicate that replacement of the benzene spacer by an anthracene moiety can not only maintain appropriate energy levels

but also enhance light harvesting properties. More rational modifications should be done to improve the overall efficiency of porphyrin-based dyes containing a carbazole donor by controlling the frontier orbital profile and extending the absorption.

Acknowledgements

J. W. acknowledges financial support from MOE Tier 2 grant (MOE2011-T2-2-130) and the IMRE Core Funding (IMRE/13-1C0205). P. W. thanks the National 973 Program (No. 2011CBA00702) and the National Science Foundation of China (No. 51203150). K.-W. H. acknowledges financial support from KAUST.

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Fig. 1. Structures of **WW-7**, **WW-8** and **YD20**.

Fig. 2. The UV-Vis absorption spectra of porphyrin dyes **WW7** (black), **WW8** (red) and **YD20** (blue) in chloroform.

Fig. 3. Cyclic voltammograms of **WW7**, **WW8** and **YD20** measured in dry DCM with TBAPF₆ as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s.

Fig. 4. Calculated HOMO and LUMO profiles and energy levels of **WW-7**, **WW-8** and **YD20** (B3LYP/6-31G*).

Fig. 5. (a) Light harvesting efficiencies (Φ_{lh}) vs wavelength (λ) for 4.2 μm -thick, dye-grafted mesoporous titania films in contact with air; (b) the corresponding photocurrent action spectra.

Fig. 6. (a) Current-voltage characteristics of the **WW-7** and **WW-8**-sensitized solar cells and the **YD20**; (b) Open-circuit photovoltage plotted as a function of short-circuit photocurrent density.

Fig. 7. (a) Plots of open-circuit photovoltage versus extracted charge. (b) Plots of lifetime of photoinjected electrons in titania as a function extracted charge.

Scheme 1. Synthetic route of porphyrin sensitizers **WW-7** and **WW-8**. Reagents and conditions: (a) NBS, FeCl₃ (cat.), chloroform, reflux, 3h; (b) i) trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuI, Et₃N/THF, reflux, 24h; ii) K₂CO₃, methanol; (c) i) Pd(PPh₃)₂Cl₂, CuI, Et₃N/THF, reflux, 12h; ii) TBAF, THF; (d) 4-iodobenzoic acid, Pd₂(dba)₃, AsPh₃, Et₃N/THF, reflux, 4h.

Table 1. Summary of optical and electrochemical properties of **WW-7**, **WW-8** and **YD20**.

Dye	λ_{abs} (nm)	ϵ (M ⁻¹ cm ⁻¹)	$E_{\text{g}}^{\text{opt}}$ (eV)	$E_{1/2}^{\text{ox}}$ (V)	$E_{1/2}^{\text{red}}$ (V)	HOMO (eV)	LUMO (eV)	E_{g}^{EC} (eV)
WW-7	454	186000	1.73	0.45	-1.30	-5.20	-3.74	1.46
				0.59	-1.63			
				1.02	-1.82			
				1.22				
WW-8	664	69000	1.86			-5.24	-3.36	1.78
	452	416000		0.43	-1.65			
	644	64500		0.85				
YD20	457	221000	1.79	0.33	-1.60	-5.02	-3.38	1.64
	667	56000		0.54				

Table 2. Photovoltaic parameters of cells measured at various irradiances (G) of simulated AM1.5 sunlight.

dye	$j_{\text{CAL}}^{\text{IPCE}}$ [mA cm ⁻²]	j_{sc} [mA cm ⁻²]	V_{oc} [V]	FF	PCE
WW7	13.43	13.54	0.829	0.683	7.7
WW8	8.02	8.15	0.749	0.760	4.6
YD20	12.05	12.93	0.774	0.657	6.6

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

- Two new push-pull type porphyrin dyes with different donors were synthesized.
- Dye with diphenyl amino-anthryl as donor showed improved light harvesting.
- Dye with diphenyl amino-anthryl as donor showed highest performance.

*Electronic Supplementary Information for***Push-Pull Type Porphyrin Based Sensitizers: the Effect of Donor Structure on the Light-Harvesting Ability and Photovoltaic Performance**

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1. Synthetic Procedures and Characterization data.

A mixture of *N*-bromosuccinimide (71.8 mg, 0.403 mmol), compound **1** (163.5 mg, 0.403 mmol), FeCl₃ (3.2 mg, 0.02 mmol) in CHCl₃ (20 mL) was refluxed under argon for 3h. Then after cooling down to room temperature, the mixture was filtrated and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, Hexane/ DCM = 1:1) to afford compound **2** (191 mg, 98%) as orange color solid. ¹H NMR (500 MHz, CDCl₃): δ ppm 8.60 (d, 2H, *J* = 9 Hz), 8.18 (d, 2H, *J* = 9 Hz), 7.58 (t, 2H, *J* = 7.5 Hz), 7.43 (t, 2H, *J* = 7.5 Hz), 6.96 (d, 4H, *J* = 9 Hz), 6.72 (d, 4H, *J* = 9 Hz), 3.72 (s, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ ppm 154.01, 141.82, 138.44, 131.89, 131.53, 128.41, 127.19, 126.76, 124.98, 122.02,

121.16, 114.58, 55.46. HR MS: calcd for $C_{28}H_{22}BrNO_2$ $[M+1]^+$ m/z 484.0912, found 484.0904.

Compound **2** (485 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, 2.5%), Et_3N (10 mL) and CuI (9 mg, 5%) were combined in THF (10 mL). After degassing and refill of argon, trimethylsilylacetylene (0.43 mL, 3 mmol) was added. Then the reaction was refluxed for 24h. After cooling to room temperature, the reaction mixture was diluted with chloroform and passed through a short column with silica gel eluted with chloroform. After removal of solvent, the residue was dissolved in DCM/Hexane (1:3) mixture and passed through a column with silica gel column eluted with the same solvent. The organic solvent was removed by rotary evaporation and afforded a crude product. The crude product was dissolved in 40 mL of THF and added dropwise into a stirred solution of K_2CO_3 (0.069 g, 0.5 mmol) in methanol (10 mL). The resulting mixture was stirred at room temperature for 4h, poured into water, extracted with ether, and the organic fraction was washed successively with water, conc. NH_4Cl solution, water and brine, and dried over Na_2SO_4 . After removal of solvent, the residue was purified by column chromatography (silica gel, Hexane/DCM = 2:1) to give compound **3** as a red solid (55% yield). 1H NMR (300 MHz, $CDCl_3$) δ ppm 8.65 (d, 2H, $J = 9.0$ Hz), 8.16 (d, 2H, $J = 9.0$ Hz), 7.56 (t, 2H, $J = 7.50$ Hz), 7.42 (t, 2H, $J = 7.50$ Hz), 6.96 (d, 4H, $J = 9.0$ Hz), 6.72 (d, 4H, $J = 9.0$ Hz), 4.04 (s, 1H), 3.72 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 154.03, 141.97, 139.48, 134.43, 130.27, 127.25, 126.76, 126.68, 125.01, 121.31, 115.68, 114.58, 88.73, 80.36, 55.47. HR MS: calcd for $C_{30}H_{23}NO_2$ $[M+1]^+$ m/z 429.1729, found 429.1733.

WW-7

Compound **3** (25 mg, 0.058 mmol), compound **4** (60 mg, 0.046 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (6.5 mg, 0.009 mmol) and CuI (3.5 mg, 0.018 mmol) were combined in THF/ Et_3N (5 mL/2.5mL). The reaction was degassed by passing a stream of argon gas for 30 mins. Then the reaction was refluxed under argon for 12h. After cooling down to the room temperature, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (silica gel, Hexane / CHCl_3 = 3 / 1) to yield a crude product. To a solution of the crude product in dry THF (10 mL) was added TBAF (0.4 mL, 1M in THF). The solution was stirred at room temperature for 30 min under argon followed by quenching with H_2O and then extracted with CH_2Cl_2 . The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue and 4-iodobenzoic acid (75 mg, 0.3 mmol) were dissolved in a mixture of dry THF (15 mL) and NEt_3 (3 mL) and the solution was degassed with argon for 15 min. $\text{Pd}_2(\text{dba})_3$ (20 mg, 0.023 mmol) and AsPh_3 (45 mg, 0.15 mmol) were added to the mixture and the solution was refluxed for 4 h under argon. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, $\text{DCM}/\text{CH}_3\text{OH}$ = 10/1) to give WW-7 (64 mg, 45%) as a green solid. ^1H NMR (500 MHz, THF-d_8) δ ppm 9.87 (d, 2H, J = 4.5 Hz), 9.62 (d, 2H, J = 4.5Hz), 9.42 (d, 2H, J = 9.0 Hz), 8.84 (d, 2H, J = 4.5Hz), 8.81 (d, 2H, J = 4.5Hz), 8.32 (d, 2H, J = 8.5 Hz), 8.22 (d, 2H, J = 8.0 Hz), 8.10 (d, 2H, J = 8.0 Hz), 7.69-7.76 (m, 4H), 7.53 (t, 2H, J = 7.5 Hz), 7.09 (d, 4H, J = 9.0 Hz), 7.05 (d, 4H, J =

9.0 Hz), 6.76 (d, 4H, 9.0 Hz), 3.90 (t, 8H, $J = 3.5$ Hz), 3.69 (s, 6H), 0.88-0.96 (m, 16H), 0.62-0.79 (m, 32H), 0.54 (t, 12H, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, THF- d_8): δ ppm 160.92, 155.38, 152.35, 152.24, 151.57, 151.56, 142.99, 139.68, 135.32, 132.65, 132.47, 131.75, 130.68, 130.58, 128.73, 127.38, 127.37, 126.13, 122.12, 121.59, 119.52, 116.55, 115.28, 107.02, 105.44, 100.72, 99.51, 95.43, 93.10, 68.99, 55.45, 32.33, 29.71, 29.65, 29.63, 26.23, 23.11, 14.11. HR MS: calcd for $\text{C}_{103}\text{H}_{110}\text{N}_5\text{O}_8 \text{ Zn}$ $[\text{M}+1]^+$ m/z 1608.7640; found, 1608.7598 (error = - 2.7 ppm). Anal. Calcd for: $\text{C}_{103}\text{H}_{109}\text{N}_5\text{O}_8 \text{ Zn}$: C, 76.82; H, 6.82; N, 4.35%. Found: C, 76.80; H, 6.85; N, 4.29%.

A similar procedure for WW-7 was employed to synthesize WW-8 (70 mg, 40%) starting from compound **5** to afford a green solid. ^1H NMR (500 MHz, THF- d_8): δ ppm 9.66 (d, 2H, $J = 9.0$ Hz), 9.61 (d, 2H, $J = 9.0$ Hz), 8.79 (br, 4H), 8.28 (d, 2H, $J = 8.0$ Hz), 8.23 (s, 2H), 8.22 (d, 2H, $J = 8.0$ Hz), 8.09 (d, 2H, $J = 8.0$ Hz), 7.83 (d, 2H, $J = 8.0$ Hz), 7.72 (t, 2H, $J = 8.5$ Hz), 7.54 (m, 4H), 7.08 (d, 4H, $J = 8.5$ Hz), 3.91 (t, 8H, $J = 6.0$ Hz), 1.48 (s, 18H), 0.96-0.99 (m, 8H), 0.92-0.95 (m, 8H), 0.71-0.83 (m, 32H), 0.63 (t, 12H, $J = 7.0$ Hz). ^{13}C NMR (75 MHz, THF- d_8): δ ppm 160.90, 152.25, 152.13, 151.55, 151.49, 143.67, 139.97, 138.85, 133.62, 132.76, 132.64, 131.74, 130.68, 127.49, 124.66, 124.34, 121.60, 117.03, 116.23, 109.98, 105.42, 100.30, 99.28, 97.75, 95.33, 35.28, 32.38, 32.25, 29.73, 29.66, 29.63, 26.23, 23.17, 14.19. HR MS: calcd for $\text{C}_{101}\text{H}_{116}\text{N}_5\text{O}_6 \text{ Zn}$ $[\text{M}+1]^+$ m/z 1558.8212; found, 1558.8265 (error = + 3.4 ppm). Anal. Calcd for $\text{C}_{101}\text{H}_{115}\text{N}_5\text{O}_6 \text{ Zn}$: C, 77.74; H, 7.43; N, 4.49%. Found: C, 77.66; H, 7.48; N, 4.43%.

2. HR mass spectra, ^1H NMR and ^{13}C NMR spectra **Figure S1.** HR mass spectrum (APCI) of compound 2.

Figure S2. HR mass spectrum (APCI) of compound 3.

Figure S3. HR mass spectrum (APCI) of compound WW-7.

Figure S5. ^1H NMR spectrum (500 MHz) of compound **2** in CDCl_3 at 298 K. **Figure S6.** ^{13}C NMR spectrum (125 MHz) of compound **2** in CDCl_3 at 298 K.

Figure S7. ^1H NMR spectrum (500 MHz) of compound **3** in CDCl_3 at 298 K. **Figure S8.** ^{13}C NMR spectrum (75 MHz) of compound **3** in CDCl_3 at 298 K.

Figure S9. ^1H NMR spectrum (500 MHz) of WW-7 in THF- d_8 at 298 K. **Figure S10.** ^{13}C NMR spectrum (125 MHz) of WW-7 in THF- d_8 at 298 K. **Figure S11.** ^1H NMR spectrum (500 MHz) of WW-8 in THF- d_8 at 298 K.

Figure S12. ^{13}C NMR spectrum (75 MHz) of WW-8 in THF-d_8 at 298 K.

3. TD-DFT calculations of WW-7 and WW-8.

Time-dependent DFT (TD-DFT) calculations have been performed at B3LYP level of theory with 6-31G* for non-metal atoms and LANL2DZ for Zn [1] as implemented in the Gaussian 09 program package [2]. The geometries of WW-7 and WW-8 were fully optimized in gas phase using the default convergence criteria without any constraints and confirmed by frequency calculations. UV-vis-NIR absorption spectra were generated assuming an average UV-vis width of 4000 cm^{-1} at half-height using the SWizard program.⁵

Table S1. Energy levels of compound WW-7

	Hartree	eV
LUMO+5	-0.01559	-0.42
LUMO+4	-0.02292	-0.62

LUMO+3	-0.05119	-1.39
LUMO+2	-0.06834	-1.86
LUMO+1	-0.07512	-2.04
LUMO	-0.09345	-2.54
HOMO	-0.16609	-4.52
HOMO-1	-0.1785	-4.86
HOMO-2	-0.18759	-5.10
HOMO-3	-0.19646	-5.35
HOMO-4	-0.21773	-5.92
HOMO-5	-0.21839	-5.94
HOMO-6	-0.21982	-5.98
HOMO-7	-0.22455	-6.11
HOMO-8	-0.22524	-6.13
HOMO-9	-0.2571	-7.00

Table S2 Selected TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength and compositions of major electronic transitions of WW-7

Wavelength (nm)	Osc. Strength (<i>f</i>)	Major contributions
725	0.7932	H-0->L+0(+95%)
609.8	0.3291	H-1->L+0(+88%) H-2->L+1(+10%)
553.7	0.0564	H-0->L+2(+83%) H-3->L+0(7%)
527.9	0.0322	H-0->L+1(+46%) H-1->L+1(+31%) H-2->L+0(21%)
501.6	0.1110	H-3->L+0(+81%) H-2->L+1(+10%)
475.6	0.1146	H-1->L+2(+83%) H-2->L+1(8%)

448.4	0.2570	H-1->L+1(+44%)	
		H-2->L+0(+26%)	
		H-2->L+2(+18%)	H-3->L+1(8%)
434.4	0.3009	H-0->L+3(+77%)	
		H-2->L+1(+8%)	
428.2	0.0223	H-2->L+2(+67%)	
		H-3->L+1(+27%)	
412.5	0.3072	H-1->L+1(5%)	
411.6	0.8976	H-5->L+0(+74%)	
		H-2->L+1(10%)	
		H-2->L+1(+28%)	
406.6	0.2704	H-5->L+0(+24%)	
		H-0->L+3(11%)	H-1->L+3(8%)
373.0	0.1138	H-9->L+0(6%)	H-3->L+0(6%)
		H-3->L+1(+56%)	
363.4	0.2743	H-2->L+2(14%)	
		H-2->L+0(+10%)	
		H-2->L+3(+9%)	
		H-1->L+3(+35%)	
		H-13->L+0(+23%)	
		H-9->L+0(+17%)	
		H-2->L+1(+11%)	
		H-2->L+3(+79%)	H-9->L+1(6%)

Figure S13. Calculated absorption spectrum for WW-7

Table S3. Energy levels of compound WW-8

	Hartree	eV
LUMO+5	-0.01717	-0.47
LUMO+4	-0.0236	-0.64
LUMO+3	-0.03417	-0.93
LUMO+2	-0.05632	-1.53
LUMO+1	-0.07677	-2.09
LUMO	-0.09415	-2.56
HOMO	-0.17608	-4.79
HOMO-1	-0.18926	-5.15
HOMO-2	-0.19352	-5.27
HOMO-3	-0.20641	-5.62
HOMO-4	-0.21905	-5.96
HOMO-5	-0.2197	-5.98
HOMO-6	-0.2212	-6.02

HOMO-7	-0.22601	-6.15
HOMO-8	-0.22666	-6.17
HOMO-9	-0.23723	-6.46

Table S4. Selected TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength and compositions of major electronic transitions of WW-8

Wavelength (nm)	Osc. Strength (<i>f</i>)	Major contributions
626.0	0.9566	H-0->L+0(+87%)
509.8	0.0820	H-1->L+1(+13%) H-2->L+0(+91%) H-1->L+1(+7%)
445.0	0.3293	H-0->L+1(+39%) H-2->L+1(29%) H-1->L+0(+29%)
425.2	0.9988	H-0->L+2(+48%) H-1->L+1(32%) H-2->L+0(+6%) H-0->L+0(+6%)
414.4	0.2854	H-4->L+0(+63%) H-2->L+1(+16%) H-1->L+1(+6%)
413.6	0.7599	H-2->L+1(+25%) H-1->L+1(17%) H-0->L+2(15%) H-5->L+0(14%) H-6->L+0(+8%) H-1->L+0(+6%)
412.7	0.4298	H-4->L+0(+36%)

		H-2->L+1(22%)	
		H-6->L+0(+9%)	H-0->L+2(9%)
		H-1->L+1(8%)	H-1->L+0(6%)
410.9	0.0702	H-5->L+0(+84%)	
377.6	0.1423	H-1->L+2(+89%)	
372.9	0.0195	H-9->L+0(+94%)	
337.5	0.1200	H-14->L+0(+59%)	
		H-9->L+1(28%)	
		H-13->L+0(+9%)

Figure S14. Calculated absorption spectrum for WW-8

Table S5. Energy levels of reference YD20.

	Hartree	eV
LUMO+5	-0.01296	-0.35
LUMO+4	-0.01573	-0.43

LUMO+3	-0.02568	-0.70
LUMO+2	-0.05104	-1.39
LUMO+1	-0.07121	-1.94
LUMO	-0.0875	-2.38
HOMO	-0.1645	-4.48
HOMO-1	-0.1831	-4.98
HOMO-2	-0.18357	-5.00
HOMO-3	-0.21494	-5.85
HOMO-4	-0.21553	-5.86
HOMO-5	-0.21613	-5.88
HOMO-6	-0.22195	-6.04
HOMO-7	-0.22264	-6.06
HOMO-8	-0.2297	-6.25
HOMO-9	-0.23122	-6.29

Table S6. Selected TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength and compositions of major electronic transitions of YD20

Wavelength (nm)	Osc. Strength (<i>f</i>)	Major contributions
659.8	1.1508	H-0->L+0(+93%)
486.9	0.1192	H-2->L+1(+7%) H-1->L+1(+37%) H-0->L+1(+33%) H-2->L+0(+29%)
437.8	0.0661	H-0->L+2(+88%)
419.3	2.1382	H-2->L+1(+59%) H-1->L+0(+11%) H-0->L+3(+9%) H-0->L+2(+5%) H-1->L+2(+5%)
418.5	0.5000	H-1->L+1(+52%)

		H-2->L+0(28%)
		H-2->L+2(11%)
		H-0->L+1(6%)
375.9	0.2397	H-2->L+2(+84%)
368.8	0.0278	H-10->L+0(+73%) H-3->L+1(10%)
		H-9->L+0(8%)
367.6	0.0104	H-1->L+2(+68%)
		H-0->L+3(16%)
		H-12->L+0(7%)
357.1	0.0114	H-0->L+3(+52%)
		H-11->L+0(+21%)
349.1	0.0111	H-1->L+2(+12%)
		H-0->L+4(+86%)
		H-1->L+4(+11%)
336.6	0.0802	H-13->L+0(+45%)
		H-9->L+1(33%)
323.1	0.1447	H-12->L+0(+9%)
		H-0->L+6(+24%)
		H-13->L+0(+23%)
313.9	0.1253	H-0->L+5(14%)
313.0	0.0256	H-12->L+0(11%)
		H-11->L+0(+6%)
		H-9->L+1(+6%)
		H-0->L+7(+85%)
		H-1->L+7(+9%)
		H-2->L+3(+48%)
		H-12->L+1(23%)
		H-11->L+1(19%)

Figure S15. Calculated absorption spectrum for YD20

Reference:

- [1] (a) Ditchfie, R. W.; Hehre, J.; Pople, J. A. Self - Consistent Molecular - Orbital Methods. IX. An Extended Gaussian - Type Basis for Molecular - Orbital Studies of Organic Molecules. *J. Chem. Phys* **1971**; 54: 724-8.
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- (5) Gorelsky, S. I., *SWizard program*, <http://www.sg-chem.net/>, University of Ottawa, Ottawa, Canada, **2010**.

5. Appendix: Cartesian coordinates of WW-7, WW-8 and YD20

WW-7

Zn	2.86190000	0.85280000	-0.80760000
N	0.90740000	0.24430000	-0.50920000
C	0.00830000	-0.11550000	-1.49010000
C	0.26530000	0.11690000	0.69100000
C	-1.24580000	-0.48300000	-0.87220000
C	-1.08740000	-0.33960000	0.47380000
H	-1.81130000	-0.52350000	1.25470000
N	2.62200000	0.62550000	-2.84960000
C	1.47170000	0.23030000	-3.49430000
C	3.55890000	0.87630000	-3.81540000
C	1.69920000	0.23850000	-4.92060000
C	2.98710000	0.64130000	-5.11930000
H	3.50290000	0.78330000	-6.05840000
N	3.10350000	1.07360000	1.23520000
C	4.24830000	1.49240000	1.87880000
C	2.16360000	0.83670000	2.19920000
C	4.00870000	1.51660000	3.30420000
C	2.72230000	1.11180000	3.50190000
H	4.73450000	1.80560000	4.05100000
H	2.19170000	1.00600000	4.43740000
N	4.81410000	1.46930000	-1.10600000
C	5.46400000	1.57300000	-2.30630000
C	5.71620000	1.81610000	-0.12600000
C	6.82660000	1.99350000	-2.08600000

C	6.98080000	2.14870000	-0.73960000
H	7.56590000	2.13510000	-2.86160000
C	0.83570000	0.38930000	1.96350000
C	5.46210000	1.83860000	1.25980000
C	0.25720000	-0.12360000	-2.87350000
C	4.89220000	1.30710000	-3.57940000
C	0.00510000	0.19710000	3.09970000
C	5.72560000	1.48610000	-4.71680000
C	-0.87030000	-0.54440000	-3.76970000
C	-1.79470000	0.40030000	-4.25320000
C	-1.02300000	-1.89230000	-4.14460000
C	-2.84890000	0.01140000	-5.09270000
C	-2.07370000	-2.29140000	-4.98350000
C	-2.97170000	-1.33110000	-5.44520000
H	-3.56200000	0.73570000	-5.46670000
H	-2.19440000	-3.32790000	-5.27370000
H	-3.78720000	-1.63650000	-6.09540000
C	6.58810000	2.26790000	2.15390000
C	6.74590000	3.62110000	2.50740000
C	7.50720000	1.32720000	2.65500000
C	7.79550000	4.02900000	3.34340000
C	8.56080000	1.72500000	3.49120000
C	8.68820000	3.07230000	3.82290000
H	7.91960000	5.06940000	3.61780000
H	9.26990000	1.00370000	3.87830000
H	9.50310000	3.38460000	4.47060000
H	-2.12850000	-0.80730000	-1.40470000
H	0.96430000	-0.02230000	-5.66880000
H	7.86980000	2.45240000	-0.20540000
O	-1.58100000	1.68420000	-3.84670000

O	-0.09000000	-2.74720000	-3.63630000
O	5.81800000	4.47190000	1.98300000
O	7.28960000	0.03810000	2.26790000
C	-2.46970000	2.69520000	-4.29310000
C	-0.17540000	-4.12250000	-3.97130000
C	5.90810000	5.85170000	2.29700000
C	8.17890000	-0.96790000	2.72410000
H	-3.49750000	2.50800000	-3.95510000
H	-2.10810000	3.62460000	-3.84960000
H	-2.46020000	2.78770000	-5.38710000
H	-1.11690000	-4.56620000	-3.62130000
H	-0.08200000	-4.28110000	-5.05370000
H	0.66130000	-4.60420000	-3.46250000
H	6.85270000	6.28610000	1.94370000
H	5.07530000	6.32910000	1.77770000
H	5.81150000	6.02750000	3.37650000
H	9.20620000	-0.78430000	2.38280000
H	8.17100000	-1.04860000	3.81910000
H	7.81680000	-1.90210000	2.29130000
C	6.43750000	1.63550000	-5.69720000
C	-0.70890000	0.03110000	4.07440000
C	7.26020000	1.80590000	-6.84010000
C	8.91030000	2.15090000	-9.14380000
C	-1.54260000	-0.16270000	5.20600000
C	-1.03310000	-0.00720000	6.51340000
C	-2.90080000	-0.52410000	5.05290000
C	-1.85510000	-0.18990000	7.61840000
H	0.01300000	0.24840000	6.64790000
C	-3.71130000	-0.71430000	6.16180000
H	-3.30330000	-0.65360000	4.05330000

C	-3.20700000	-0.53480000	7.45950000
H	-1.41440000	-0.09950000	8.60920000
H	-4.75110000	-1.00240000	6.04870000
C	-4.14200000	-0.75870000	8.60560000
O	-5.17930000	-1.37300000	8.50940000
O	-3.78080000	-0.22840000	9.80810000
H	-3.01940000	0.36330000	9.69650000
N	9.73830000	2.32360000	-10.29750000
C	11.10900000	1.95130000	-10.22910000
C	11.50870000	0.85020000	-9.44970000
C	12.10050000	2.67580000	-10.90560000
C	12.84760000	0.49580000	-9.35090000
H	10.76090000	0.27090000	-8.91820000
C	13.44590000	2.30930000	-10.82700000
C	13.83080000	1.21600000	-10.04310000
H	13.15410000	-0.35300000	-8.74740000
H	14.17980000	2.89470000	-11.36960000
C	9.16740000	2.85790000	-11.48550000
C	8.16120000	3.83840000	-11.41080000
C	9.56140000	2.41130000	-12.75470000
C	7.57260000	4.34430000	-12.56210000
H	7.84000000	4.20250000	-10.44050000
C	8.98790000	2.93350000	-13.91620000
C	7.98270000	3.90290000	-13.82770000
H	6.79440000	5.09890000	-12.50250000
H	9.32460000	2.56310000	-14.87800000
C	7.72060000	4.05030000	-16.19600000
H	7.10170000	4.62360000	-16.88910000
H	8.78000000	4.25610000	-16.40270000
H	7.52950000	2.97840000	-16.34310000

C	16.14520000	1.47390000	-10.56850000
H	17.07550000	0.96090000	-10.31660000
H	16.00270000	1.44940000	-11.65780000
H	16.20970000	2.52040000	-10.24020000
O	7.34900000	4.47460000	-14.89710000
O	15.11700000	0.77470000	-9.89090000
H	10.32910000	1.64900000	-12.84030000
H	11.82080000	3.53520000	-11.50640000
C	9.09640000	2.98610000	-8.01580000
C	10.07080000	4.03350000	-8.00540000
C	8.26850000	2.80980000	-6.84910000
C	10.23190000	4.84320000	-6.91110000
H	10.68560000	4.17780000	-8.88520000
C	8.46640000	3.67800000	-5.73390000
C	9.42170000	4.66150000	-5.75780000
H	10.97760000	5.63340000	-6.92670000
H	7.82800000	3.55240000	-4.86560000
H	9.55360000	5.31190000	-4.89740000
C	7.91330000	1.14580000	-9.13920000
C	7.07540000	0.97280000	-7.97910000
C	7.72680000	0.26260000	-10.24910000
C	6.09230000	-0.06170000	-7.99470000
C	6.76680000	-0.71560000	-10.22570000
H	8.36310000	0.37950000	-11.11770000
C	5.93560000	-0.87890000	-9.08470000
H	5.47740000	-0.19950000	-7.11180000
H	6.64480000	-1.37570000	-11.08020000
H	5.18150000	-1.66110000	-9.07340000

Zn	2.78120000	0.81510000	-0.74540000
N	0.91560000	-0.00810000	-0.40000000
C	0.08420000	-0.56600000	-1.34700000
C	0.27340000	-0.10030000	0.80350000
C	-1.12670000	-1.02440000	-0.70410000
C	-1.00960000	-0.73780000	0.62330000
H	-1.71930000	-0.93450000	1.41410000
N	2.60370000	0.37430000	-2.75870000
C	1.53190000	-0.24010000	-3.36590000
C	3.52460000	0.63590000	-3.73690000
C	1.79570000	-0.36790000	-4.78070000
C	3.02630000	0.17310000	-5.00950000
H	3.55570000	0.25600000	-5.94790000
N	2.95900000	1.25590000	1.26810000
C	4.03230000	1.87100000	1.87520000
C	2.04000000	0.99300000	2.24570000
C	3.76840000	1.99720000	3.29070000
C	2.53880000	1.45530000	3.51940000
H	4.44030000	2.44350000	4.01000000
H	2.01000000	1.37140000	4.45810000
N	4.64670000	1.63900000	-1.09060000
C	5.28990000	1.72920000	-2.29530000
C	5.47780000	2.19630000	-0.14520000
C	6.57230000	2.36530000	-2.11470000
C	6.68890000	2.65330000	-0.78700000
H	7.28270000	2.55970000	-2.90540000
C	0.78340000	0.36040000	2.04690000
C	5.20340000	2.30910000	1.23180000
C	0.35830000	-0.67860000	-2.72170000
C	4.78120000	1.26730000	-3.53850000

C	-0.03480000	0.17080000	3.19270000
C	5.60300000	1.45330000	-4.68370000
C	-0.69320000	-1.32060000	-3.57820000
C	-1.69120000	-0.54080000	-4.19220000
C	-0.70270000	-2.71310000	-3.78260000
C	-2.67870000	-1.13480000	-4.99170000
C	-1.68600000	-3.31680000	-4.58020000
C	-2.66040000	-2.51630000	-5.17290000
H	-3.44890000	-0.53800000	-5.46480000
H	-1.69660000	-4.38810000	-4.73900000
H	-3.42410000	-2.98030000	-5.79130000
C	6.25640000	2.95040000	2.08720000
C	6.26610000	4.34260000	2.29340000
C	7.25670000	2.17020000	2.69700000
C	7.25120000	4.94570000	3.08910000
C	8.24630000	2.76350000	3.49450000
C	8.22780000	4.14470000	3.67780000
H	7.26170000	6.01680000	3.24960000
H	9.01810000	2.16640000	3.96450000
H	8.99300000	4.60820000	4.29480000
H	-1.95440000	-1.50270000	-1.20790000
H	1.12390000	-0.81440000	-5.49990000
H	7.51680000	3.13120000	-0.28300000
O	-1.61520000	0.79850000	-3.94820000
O	0.29510000	-3.40000000	-3.15680000
O	5.26620000	5.03010000	1.67140000
O	7.18070000	0.83130000	2.45130000
C	-2.58340000	1.65230000	-4.53540000
C	0.35160000	-4.80860000	-3.31220000
C	5.21010000	6.43840000	1.82820000

C	8.15250000	-0.02270000	3.03200000
H	-3.59770000	1.41040000	-4.19180000
H	-2.32410000	2.66160000	-4.21120000
H	-2.55250000	1.60440000	-5.63190000
H	-0.55250000	-5.29470000	-2.92270000
H	0.49110000	-5.09400000	-4.36320000
H	1.21580000	-5.13640000	-2.73190000
H	6.11320000	6.92500000	1.43680000
H	4.34450000	6.76680000	1.25040000
H	5.07350000	6.72300000	2.87980000
H	9.16500000	0.22160000	2.68450000
H	8.12640000	0.02220000	4.12880000
H	7.89320000	-1.03150000	2.70620000
C	6.31080000	1.61450000	-5.66310000
C	-0.73660000	0.00640000	4.17640000
C	6.74340000	1.33860000	-8.07380000
C	7.13990000	1.80290000	-6.80160000
C	7.55250000	1.52930000	-9.18720000
C	8.38440000	2.45930000	-6.69030000
C	8.79190000	2.17510000	-9.06200000
C	9.20050000	2.63470000	-7.80080000
C	-1.55340000	-0.18590000	5.32070000
C	-1.12450000	0.24820000	6.59370000
C	-2.81080000	-0.82340000	5.21640000
C	-1.93000000	0.06570000	7.71080000
H	-0.15240000	0.72040000	6.69330000
C	-3.60350000	-1.01120000	6.33860000
H	-3.14900000	-1.16910000	4.24470000
C	-3.18410000	-0.55600000	7.59850000
H	-1.54710000	0.37850000	8.68000000

H	-4.56360000	-1.51090000	6.26470000
C	-4.09260000	-0.79660000	8.76250000
O	-4.98100000	-1.61690000	8.75600000
O	-3.88530000	-0.03440000	9.87320000
H	-3.25740000	0.67920000	9.67610000
N	9.62190000	2.35950000	-10.19420000
C	10.03150000	1.35890000	-11.08680000
C	9.76640000	-0.01300000	-11.08390000
C	10.86950000	1.93050000	-12.07200000
C	10.33420000	-0.78810000	-12.08990000
H	9.14580000	-0.46910000	-10.31970000
C	11.42480000	1.12210000	-13.07260000
C	11.16500000	-0.25020000	-13.10220000
H	10.12570000	-1.85410000	-12.08510000
H	12.06490000	1.57940000	-13.81930000
C	10.19700000	3.56960000	-10.60640000
C	10.06500000	4.85540000	-10.07570000
C	10.97310000	3.34320000	-11.76660000
C	10.73890000	5.89410000	-10.70990000
H	9.45180000	5.04770000	-9.20140000
C	11.63980000	4.41120000	-12.38140000
C	11.53960000	5.70420000	-11.86190000
H	10.63580000	6.89230000	-10.29420000
H	12.23140000	4.21630000	-13.26910000
C	12.25680000	6.91320000	-12.49240000
C	11.21180000	7.96960000	-12.92520000
C	13.22000000	7.54190000	-11.45710000
C	13.08170000	6.52310000	-13.73370000
H	10.52160000	7.55500000	-13.66900000
H	10.61470000	8.32410000	-12.07850000

H	11.70880000	8.84110000	-13.36990000
H	13.97930000	6.81780000	-11.14020000
H	13.73530000	8.40870000	-11.88970000
H	12.69010000	7.88320000	-10.56160000
H	13.57300000	7.41250000	-14.14440000
H	13.86450000	5.79560000	-13.49020000
H	12.45320000	6.09840000	-14.52490000
C	11.75130000	-1.18590000	-14.17630000
C	12.63540000	-2.26120000	-13.50000000
C	10.60120000	-1.87960000	-14.94510000
C	12.62050000	-0.43000000	-15.19930000
H	13.46940000	-1.79820000	-12.96000000
H	12.06830000	-2.86360000	-12.78240000
H	13.05290000	-2.94340000	-14.25110000
H	9.96360000	-1.14120000	-15.44460000
H	11.00350000	-2.55540000	-15.71020000
H	9.96530000	-2.47280000	-14.27940000
H	13.01380000	-1.13370000	-15.94190000
H	12.04610000	0.33230000	-15.73820000
H	13.47750000	0.05990000	-14.72310000
H	7.22350000	1.19190000	-10.16490000
H	5.78560000	0.83900000	-8.18070000
H	8.71020000	2.81630000	-5.71830000
H	10.16780000	3.11560000	-7.69630000
YD20			
Zn	2.85570000	0.83400000	-0.80420000
N	0.89520000	0.24650000	-0.50410000
C	-0.01510000	-0.08240000	-1.48650000
C	0.25840000	0.10740000	0.69730000

C	-1.27140000	-0.44060000	-0.86720000
C	-1.10290000	-0.32340000	0.48010000
H	-1.82510000	-0.50990000	1.26210000
N	2.59930000	0.65160000	-2.84870000
C	1.44510000	0.26850000	-3.49270000
C	3.53830000	0.89360000	-3.81570000
C	1.67220000	0.27230000	-4.91880000
C	2.96540000	0.65840000	-5.11780000
H	3.49080000	0.77820000	-6.05450000
N	3.11350000	1.01150000	1.24100000
C	4.27000000	1.39910000	1.88480000
C	2.17790000	0.76620000	2.20660000
C	4.04180000	1.39230000	3.31240000
C	2.75110000	1.00190000	3.51100000
H	4.77760000	1.65240000	4.06000000
H	2.22620000	0.88170000	4.44790000
N	4.81490000	1.42680000	-1.10400000
C	5.45350000	1.56150000	-2.30800000
C	5.72380000	1.75640000	-0.12510000
C	6.81250000	1.99160000	-2.09080000
C	6.97960000	2.11340000	-0.74230000
H	7.53550000	2.17260000	-2.87330000
C	0.84120000	0.34490000	1.97140000
C	5.48130000	1.74680000	1.26400000
C	0.22740000	-0.07480000	-2.87010000
C	4.87490000	1.31600000	-3.58240000
C	0.01540000	0.14280000	3.10900000
C	5.70300000	1.50760000	-4.72070000
C	-0.91090000	-0.46510000	-3.76660000
C	-1.82530000	0.50070000	-4.22700000

C	-1.08530000	-1.80370000	-4.16450000
C	-2.89080000	0.14170000	-5.06560000
C	-2.14730000	-2.17320000	-5.00300000
C	-3.03500000	-1.19250000	-5.44100000
H	-3.59640000	0.88230000	-5.42150000
H	-2.28450000	-3.20260000	-5.31050000
H	-3.85930000	-1.47490000	-6.09050000
C	6.62070000	2.14000000	2.15770000
C	6.79410000	3.47940000	2.55370000
C	7.53950000	1.17680000	2.61470000
C	7.85880000	3.85180000	3.38750000
C	8.60780000	1.53880000	3.44850000
C	8.75060000	2.87350000	3.82240000
H	7.99480000	4.88170000	3.69390000
H	9.31650000	0.79980000	3.80180000
H	9.57700000	3.15820000	4.46830000
H	-2.16220000	-0.74190000	-1.39970000
H	0.93560000	0.01450000	-5.66640000
H	7.87030000	2.41510000	-0.20970000
O	-1.59100000	1.77420000	-3.79960000
O	-0.16120000	-2.68060000	-3.67820000
O	5.86600000	4.35410000	2.07080000
O	7.30640000	-0.09750000	2.18900000
C	-2.47040000	2.80430000	-4.21900000
C	-0.26750000	-4.04800000	-4.03790000
C	5.97340000	5.72250000	2.42580000
C	8.19290000	-1.12450000	2.60060000
H	-3.49760000	2.62380000	-3.87570000
H	-2.09330000	3.72060000	-3.76160000
H	-2.46940000	2.91730000	-5.31130000

H	-1.21200000	-4.48590000	-3.68890000
H	-0.18430000	-4.18780000	-5.12380000
H	0.56660000	-4.55010000	-3.54460000
H	6.91630000	6.15960000	2.07130000
H	5.13710000	6.22290000	1.93460000
H	5.89500000	5.86590000	3.51160000
H	9.21700000	-0.93880000	2.25080000
H	8.19970000	-1.23970000	3.69260000
H	7.81670000	-2.04160000	2.14390000
C	6.41260000	1.66840000	-5.69990000
C	-0.69460000	-0.03130000	4.08550000
C	7.23520000	1.85130000	-6.84170000
C	8.88200000	2.21380000	-9.13170000
C	-1.52290000	-0.23430000	5.21890000
C	-1.00540000	-0.09810000	6.52560000
C	-2.88430000	-0.58580000	5.06960000
C	-1.82220000	-0.28940000	7.63280000
H	0.04290000	0.14970000	6.65730000
C	-3.68960000	-0.78470000	6.18070000
H	-3.29330000	-0.70080000	4.07080000
C	-3.17730000	-0.62420000	7.47790000
H	-1.37510000	-0.21390000	8.62210000
H	-4.73180000	-1.06500000	6.06990000
C	-4.10690000	-0.85580000	8.62610000
O	-5.14990000	-1.46050000	8.52900000
O	-3.73430000	-0.34380000	9.83340000
H	-2.96890000	0.24310000	9.72430000
N	9.69810000	2.39290000	-10.26410000
C	11.12060000	2.37700000	-10.14720000
C	11.77570000	1.33990000	-9.45980000

C	11.89470000	3.38250000	-10.73500000
C	13.15950000	1.32300000	-9.35540000
H	11.18940000	0.54780000	-9.00420000
C	13.28890000	3.36130000	-10.65250000
C	13.93050000	2.33120000	-9.95470000
H	13.67060000	0.52550000	-8.82510000
H	13.85630000	4.15610000	-11.12340000
C	9.12330000	2.58210000	-11.55650000
C	8.10480000	3.53000000	-11.76100000
C	9.57810000	1.84320000	-12.65350000
C	7.55320000	3.71640000	-13.02080000
H	7.74600000	4.11760000	-10.92150000
C	9.04290000	2.04020000	-13.92860000
C	8.01980000	2.97630000	-14.11850000
H	6.76570000	4.44550000	-13.18410000
H	9.42300000	1.45140000	-14.75560000
C	7.84790000	2.52110000	-16.45640000
H	7.24630000	2.88980000	-17.28940000
H	8.91060000	2.69750000	-16.67140000
H	7.67990000	1.44200000	-16.33860000
C	16.10970000	3.20790000	-10.38570000
H	17.13580000	2.92240000	-10.14650000
H	15.98950000	3.24580000	-11.47690000
H	15.90400000	4.20250000	-9.96740000
O	7.41890000	3.24420000	-15.31530000
O	15.28270000	2.21480000	-9.80340000
H	10.36430000	1.10830000	-12.51070000
H	11.40190000	4.18920000	-11.26900000
C	9.31760000	2.61970000	-7.85330000
C	8.51550000	2.43660000	-6.73700000

C	7.60630000	1.62300000	-9.24220000
C	6.80250000	1.45280000	-8.12510000
H	7.25300000	1.29190000	-10.21270000
H	5.82670000	0.98890000	-8.23360000
H	8.86990000	2.76320000	-5.76380000
H	10.29060000	3.08630000	-7.74370000