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**Rational Design of Hydrogen-Donor Solvents for Direct Coal
Liquefaction**

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Abstract

Facing the challenge of processes in direct coal liquefaction (DCL), it is vital to develop optimal hydrogen-donor solvent (H-donor) to dramatically moderate coal liquefaction conditions. Here, we propose an approach for rational design of optimal H-donor candidates based on density functional theory (DFT) calculations combining reverse searching algorithm. Firstly, the mechanism of hydrogen transfer from H-donor to coal radical was investigated by using common model compounds. DFT calculations show that the concerted hydrogen transfer route promoted by coal radicals is the dominant pathway. The C–H BDEs show strong correlation with intrinsic reaction barriers and rate constants (in log scale), which allow us to define a cheap metric for comparing the hydrogen-donation ability of different H-donors. Then the framework for rational design of H-donor candidates is established to seek molecules with low C–H BDEs based on inverse molecular design strategy. In the searching procedure, the chemical structure of parent molecule is varied by appropriate substituent from a predefined library (15 substituents). To reduce searching space, four empirical rules are proposed to guide the structural modifications. Finally, the H-donor candidates designed are validated by transition state calculations. It is confirmed that the inverse molecular design approach is effective for seeking candidate H-donors with lower reaction barriers and potentially higher rate of hydrogenation, which open a window for the rational design of optimal H-donors to improve the yields of the liquid products from coal under mild conditions.

1. Introduction

Direct coal liquefaction (DCL) is a clean and efficient technology for coal utilization, which convert solid coal (H/C ratio ≈ 0.8) to liquid fuels (H/C ratio ≈ 2) by adding hydrogen.¹ It is very vital to provide enough hydrogen timely to stabilize free radicals from coal pyrolysis for getting more liquid fuels and inhibiting coke formation in direct liquefaction process.^{2,3} Hydrogen gas and hydrogen-donor solvent (H-donor) are major hydrogen sources. Direct coal liquefaction processes, which traditionally operate at relatively high temperature and pressure, pose a lot of challenges in facility manufacturing, safe operation and economy. Consequently, considerable efforts have been directed to pursuing the moderation of reaction conditions. The obvious solution, decreasing hydrogen pressure, has unfavorable impact on oil yield. Hence, as a potential alternative, improving hydrogen-donor ability of solvent attracts broad attention.^{4,5}

In general, the hydrogen-donor ability of liquefaction solvents with different chemical structure could be ranked by coal liquefaction experiments. Kuhlmann et al.¹³ concluded that 4,5-dihdropyrene, hexahydro-pyrene and 9,10-dihydrophenanthrene were quite active and symoctahydrophenanthrene and 2a,3,4,5-tetrahydrophenanthrene were moderate activity. Curtis and coworker⁶ found that the solvents with different hydrogen-donor ability from strong to weak were, in order, cyclic olefins, hydroaromatics, cycloalkanes at 380 °C. Kamiya et al.⁷ reported that 9,10-dihydroanthracene, 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydroquinoline exhibited outstanding hydrogen-donor ability and acenaphthene and indan showed mild hydrogen-donor ability. So far, only a limited number of common hydrogen-donor solvents were evaluated experimentally, and little information is known about the relationship between hydrogen-donor ability of solvent and its molecular structure.

Molecular design based on quantitative structure-property relationship (QSPR) model provides useful support and guidance to experimental design and synthesis in search of molecules with desired physical and chemical characteristics. It has been successfully applied to design drug candidates⁸, new materials⁹ and biochemical macromolecules such as protein¹⁰. A study of structure-reactivity relationship of H-donors may help us open a window to screen and design H-donors in a rational way. However, relevant literature in the area of coal liquefaction is scarce.

To provide a basis for molecular design of H-donors, it is important to understand the hydrogen donation mechanism under coal liquefaction conditions at molecular level, but to date, it is still a matter of debate. So far, there are two distinct molecular mechanisms that have been proposed. The first is a stepwise mechanism, in which the hydrogen atom in H-donor is abstracted, forming hydrogen radical, then it unites with free radical produced from coal pyrolysis.^{11,12} The other is a concerted mechanism, which suggests that C–H bond cleavage in H-donor is assisted by coal radicals.¹³ For our knowledge, a systematical theoretical mechanism study with a state of the art method is still absent.

At present, we focus on the two vital problems in direct coal liquefaction: what is the mechanism of hydrogen donation during coal liquefaction, and how to improve hydrogen-donor ability of a H-donor by structural modifications in a systematical way. As far as we know, this is the first attempt of theoretical design of H-donor in coal liquefaction. The paper is organized as follows. In Sec. 2, we describe the computational details about C–H bond dissociation enthalpies (BDEs) and activation enthalpies. In Sec. 3, we explored the hydrogen donation mechanism and showed promising H-donor candidates can be designed in a rational way from smaller

hydroaromatic compounds. The results were discussed and the effectiveness of our strategy was validated. Finally, in Sec. 4, conclusions were drawn.

2. Computational details

Density functional theory (DFT) was used to calculate BDEs and activation barriers in this work. All DFT calculations were performed using Gaussian 09 package with default settings. Molecular geometries were obtained at B3LYP/6-311+G(d,p) level followed by frequency calculations at the same level to validate local minima and transition states. The final energies were further improved by single-point calculations at B3LYP/6-311+G(3df,2p) level. It is generally believed that a high level of theory beyond B3LYP with flexible basis set is necessary to obtain accurate thermochemistry such as BDEs.¹⁴ In this work, to be computationally affordable for large system, the newly proposed X_{3D} scheme¹⁵ were conveniently applied, which extends the B3LYP results by correcting its errors on heats of formation of hydrocarbon with three-dimension (3D) molecular descriptors without extra cost. The X_{3D} method was shown to be competitive with the coupled-cluster based G4 method for accuracy at a considerably lower computational cost.¹⁵ R-H BDEs are determined as following equation:

$$\text{BDE(R-H)} = [\Delta_f H(\text{R}^\bullet, 298\text{K}) + \Delta_f H(\text{H}^\bullet, 298\text{K})] - \Delta_f H(\text{R-H}, 298\text{K})$$

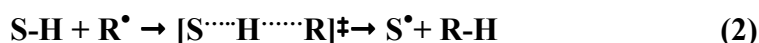
in which $\Delta_f H$ is the enthalpies of formation for each species at 298 K. It should be noted that $\Delta_f H(\text{H}^\bullet, 298\text{K})$ is based on experimental data in order to enhance calculation accuracy further. Based on our test results, the overall MAD (mean absolute deviation) of X_{3D} is only 2.6 kJ/mol (see **Table S1** in ESI for details), which should be sufficiently accurate for our molecular design purpose.

In this work, C–H BDEs by X_{3D} scheme were explicitly reported for enhancing the accuracy, while the activation barriers (298 K) were calculated at B3LYP level due to the limitation of X_{3D} scheme. We limit the molecule space to polycyclic hydroaromatic compounds containing only carbon and hydrogen elements, partially because X_{3D} model is not extended to other elements yet. Another reason is that the practical H-donors in coal liquefaction contain only C and H, since other elements such as sulfur have to be mostly removed during prehydrogenation of solvents.¹⁶

3. Results and discussion

3.1 Hydrogen-donating mechanism of H-donors.

To find a metric to measure hydrogen-donor ability of a H-donor, B3LYP calculations were carried out to explore the mechanism of hydrogen transfer reaction for coal liquefaction. In this work, hydrogen transfer reaction refers to cleavage of a C–H bond in H-donor (S-H) and forming a new C–H bond with coal radical (R[•])(see **eq. 1**). As mentioned before, there are two possible mechanisms, i.e., the stepwise and the concerted. For stepwise mechanism, the H-donor (S-H) breaks a C–H bond by forming intermediates (S[•] + H[•]), then the hydrogen radical (H[•]) reacts with coal radical (R[•]) forming product R-H (**eq. 2**). In this case, the energy barrier is effectively equal to the C–H BDE in S-H. Comparatively, if the reaction proceeds in a concerted manner, the H-donor (S-H) breaks its C–H bond through a transition state assisted by coal radical (R[•]).



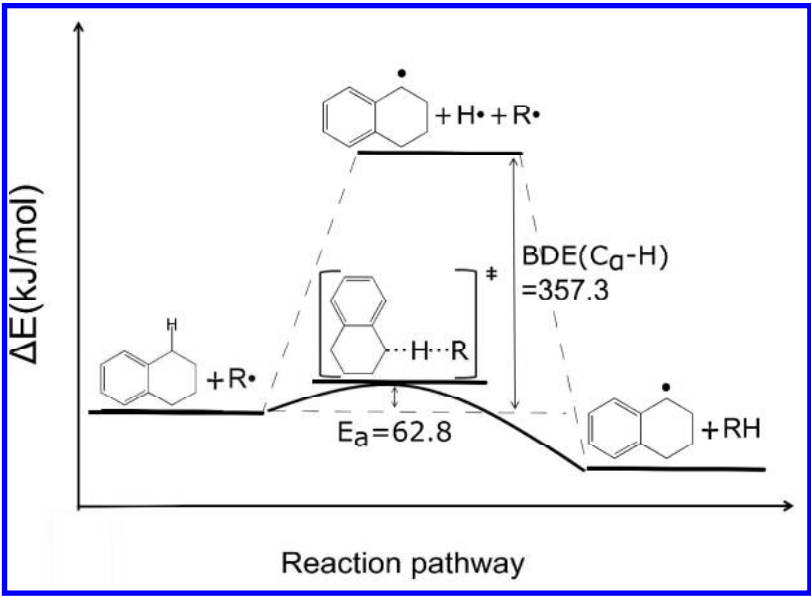
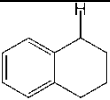
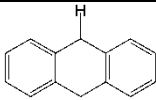
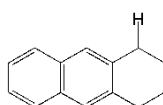
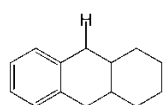
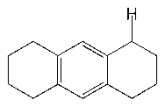
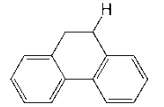
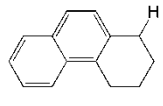
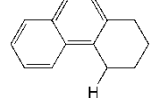
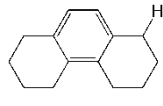
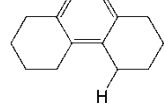
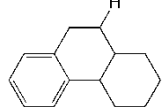
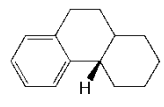
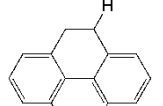
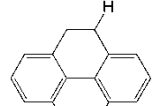
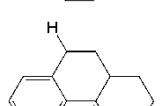
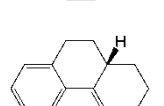
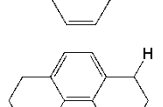
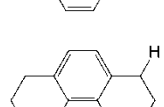
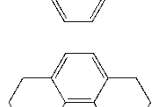
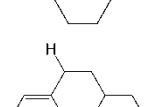
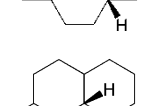
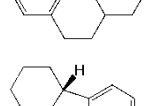
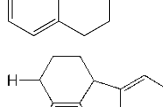
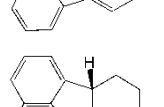
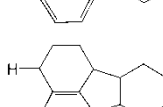
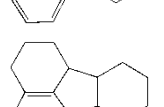
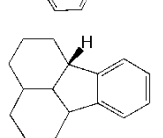


Figure 1. Hydrogen transfer from H-donor (S-H) to coal radical (R^\bullet) in stepwise and concerted mechanism (S-H: tetralin, R^\bullet : benzyl).

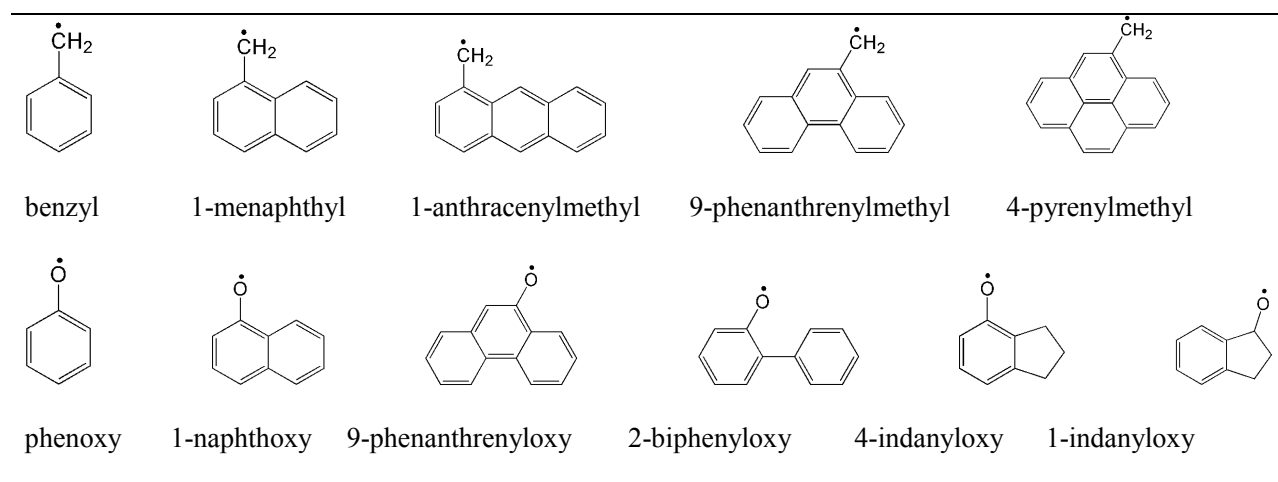
To get better understanding on which mechanism is more plausible under coal liquefaction conditions, some common H-donors and free radicals produced from coal pyrolysis were chosen as model compounds. It is well recognized that the effective hydrogen-donor species are hydroaromatics in liquefaction solvents for traditional liquefaction processes.¹⁷ As shown in **Table 1**, the BDEs of C–H at the α -carbon position ($C_\alpha-H$) for typical H-donors in coal liquefaction are in range of 310-365 kJ/mol.

Table 1. C–H BDEs of common hydroaromatics in liquefaction solvents.

Compounds	BDE(kJ/mol)	Compounds	BDE(kJ/mol)
	357.3		328.0

	352.3		357.7
	356.5		362.3
	355.6		353.5
	358.1		356.5
	356.9		350.2
	354.0		361.5
	355.2		341.4
	354.8		351.5
	336.0		354.4
	347.3		313.0
	356.9		321.7
	359.8		350.2
	358.6		

Model compounds of coal free radicals were selected based on the macromolecular structure of coal and the analysis of coal liquefaction products. Alkylaromatic and phenoxy radicals derived from cleavage of bridge bonds during coal decomposition are typical radicals.¹⁸ The aromatic nucleuses were mainly composed of benzene, naphthalene, phenanthrene in low-rank coal, and of phenanthrene, anthracene, pyrene in middle-rank coal.^{19,20} In fact, coal liquefaction products contain plenty of alkyl-substituted benzene, naphthalene, phenanthrene, anthracene, pyrene.²¹ In addition, according to the analysis of oxygenated species in coal liquefaction products, phenolic compounds are predominant, which are mainly composed of alkyl-substituted phenol, naphthol, phenanthrol, indanol, biphenylol.²² The selected coal free radicals were compiled in scheme 1.



Scheme 1. Different free radicals studied in this work.

The reaction mechanisms were investigated using tetralin and benzyl radical as model compounds of H-donor and coal free radical, respectively. As shown in **Figure 1**, the barrier

height for the stepwise pathway is 357.3 kJ/mol, which is 5 times larger than that for the concerted pathway. To assess the effect of the choice of model compounds on activation barriers in the concerted mechanism, we extended our calculations to other type of H-donors and radicals. As shown in **Figure 2(a)**, the barrier heights for tetralin toward different radicals are in a range of 10-80 kJ/mol, mainly accumulated around 70 kJ/mol, which are much lower than C_{α} -H BDE of tetralin. Meanwhile, **Figure 2(b)** presents the activation barriers of α -H transfer reactions between benzyl radical and typical hydroaromatics, which are mainly in the range of 60-70 kJ/mol.

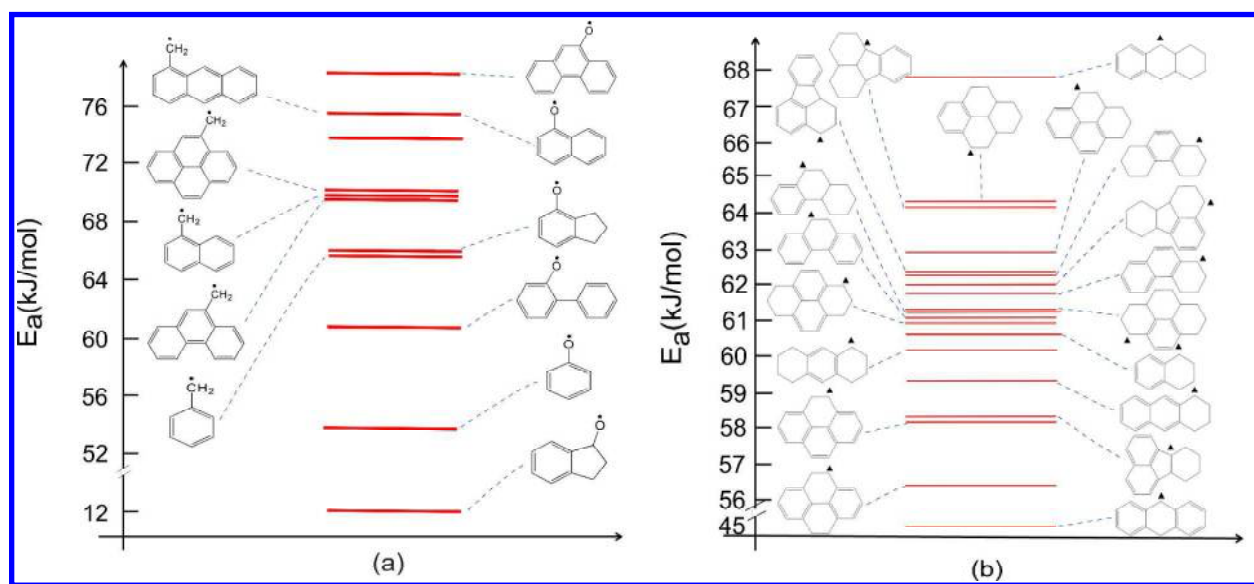


Figure 2. (a) Activation barriers for α -H transfer reactions of tetralin assisted by different radicals derived from coal pyrolysis. (b) Activation barriers for α -H transfer reactions of H-donors assisted by benzyl radical (dehydrogenation site marked by ▲)

In comparison, **Figure 3** shows statistic bar plots for barrier heights of C_{α} -H abstraction in different mechanisms for typical H-donors. It is quite clear that the average barrier height for the

concerted reaction path is substantially less than that in the stepwise reaction path. However, the reaction rate will depend not only on the apparent activation energies, but also the apparent Arrhenius pre-exponential factors. It is noted that the pre-exponential factors A for unimolecular scissions are $\sim 10^6$ times larger than typical A factors for bimolecular H transfer reactions.²³ With these facts in mind, the estimated relative reaction rate according to Arrhenius equation for the concerted pathway is about $\sim 10^{25}$ faster than in the stepwise pathway, even in the worst scenario. As a result, under liquefaction conditions, hydrogen transfer is more likely to proceed via a concerted mechanism.

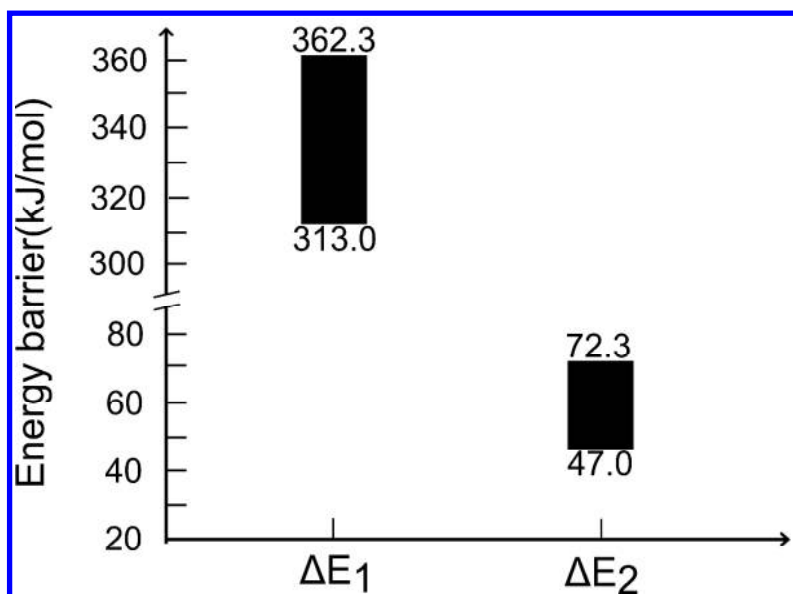


Figure 3. The ranges of BDEs of $C_\alpha-H$ for typical H-donors and the activation barriers for α -H transfer between benzyl radical and typical H-donors.

3.2 Scaling relation between activation enthalpies and C-H BDEs

As revealed in the mechanism calculations, the intrinsic reaction barriers in concerted pathway should be considered as one of the most reliable metric for evaluating hydrogen-donor

ability of a H-donor. However, the transition state calculations are usually expensive and time consuming, which will be the bottleneck of molecular design of H-donors with large molecular size. Instead of direct calculations, a practical approach is to utilize a scaling relation between activation barriers and C–H bond strength, i.e., BDEs. Similar concept such as Brønsted–Evans–Polanyi (BEP) relation is well known in theoretical design of catalysts^{24,25}, and is routinely used to correlate and predict the rate of hydrogen abstraction by hydrocarbon radicals²³.

We assume that the hydrogen-donor ability of H-donors is mainly determined by its C_α–H BDE. It is well known that α hydrogen atom is easier to be abstracted than hydrogens at other positions. Once α hydrogen in H-donor is abstracted, the C_β–H BDEs of free radicals derived from the H-donor is expected to be lower, which is supported by experimental findings of Kamiya⁷ and Senthilnathan²⁶.

To test the validity of linear relation between the C–H BDEs and the concerted reaction barriers, we compiled a list of molecules (**Scheme S1** in ESI) frequently used as model solvents in study of liquefaction solvents. To account for the entropic effects, the relation between BDE and the rate constant was also included. The reaction rate constants were estimated using DFT calculations and classic transition state theory as illustrated in literature²⁷⁻²⁹. As shown in **Figure 4**, BDEs are well correlated with the intrinsic reaction barriers ($R^2=0.98$) and logarithm of rate constants ($R^2=0.98$). The relative hydrogen-donor abilities of various H-donors toward benzyl radical have been experimentally measured. It is found that the rates of hydrogen transfer depend strongly on the C–H bond strength of the H-donor (in an approximate but not perfect inverse correlation).^{7, 30, 31} Our theoretical results are in good accordance with these findings. Hence, it is reasonable to use the C–H BDEs instead of the reaction barriers for evaluating hydrogen-donor

ability of different H-donors, which will greatly improve the efficiency of our H-donor design process.

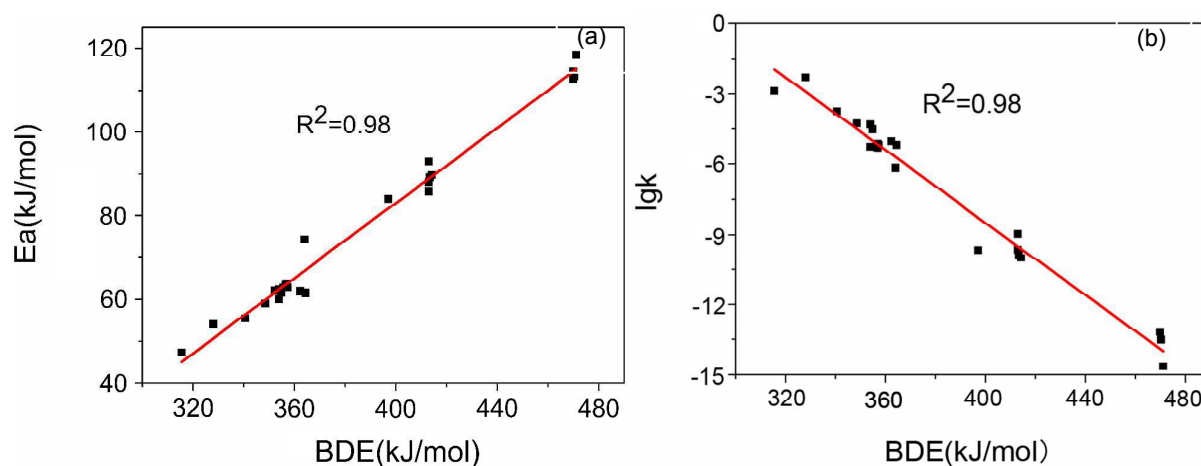


Figure 4. (a) The correlation between C_{α} -H BDEs of H-donors and the activation barriers of concerted α -H transfer reactions between benzyl radical and typical H-donors. (b) logarithm of rate constants vs. C_{α} -H BDEs.

From above analysis, we can easily understand the experimental result of Kamiya and his coworkers that the hydrogen-donor ability of the hydroaromatic hydrocarbon is governed by the lability of the benzylic C-H BDE⁷. In addition, we have evaluated the quality of several common H-donors. The evaluation is based on the kinetic test of H-donors developed by Lewis and Kleinpeter.^{32, 33} The kinetic test used 8 part H-donors to 1 part Australian lignite at 750 °F for 10 min. The high solvent/coal ratio in the kinetic test prevents the H-donor concentration from being a limiting factor. The result of evaluation shows that conversion of Australian lignite increase with the decrease of C_{α} -H BDEs of H-donors in **Figure 5**.

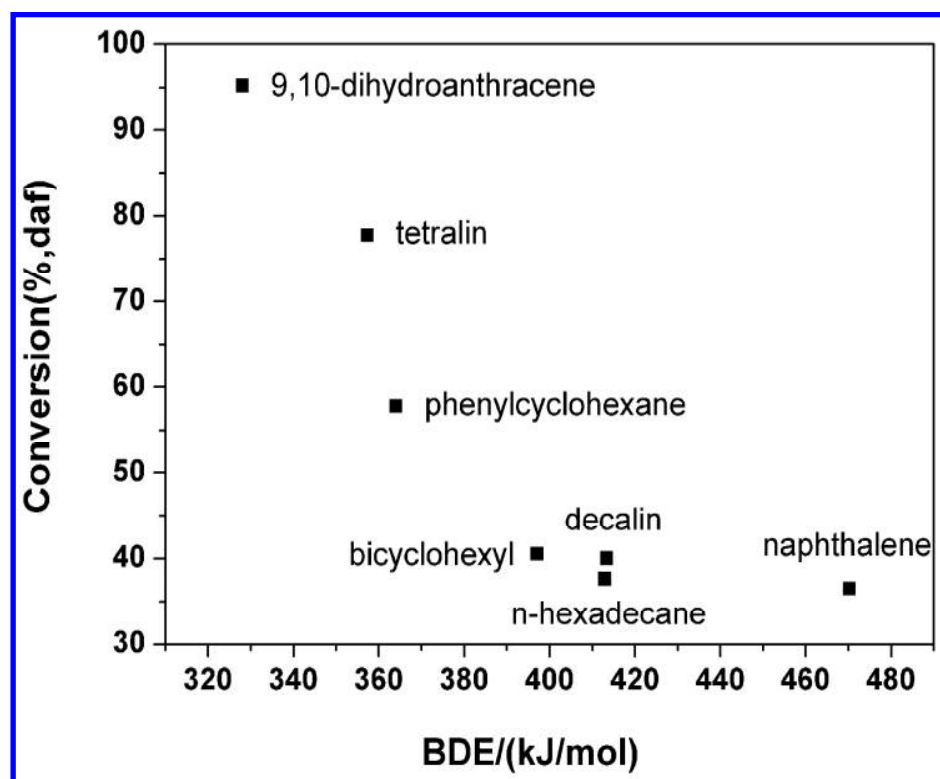


Figure 5. Conversion of Australian lignite vs. C_{α} -H BDEs of common H-donors (H-donor: naphthalene, tetralin, decalin, 9,10-dihydroanthracene, phenylcyclohexane, bicyclohexyl, n-hexadecane)

3.3 Rational design of H-donors based on C-H BDEs.

3.3.1 Variable depth search (VDS) algorithm for inverse design of optimal H-donors.

Theoretical modeling is well established for calculating properties from molecular structures. The inverse molecular design generally searches molecules with optimized properties.³⁴ There are lots of impressive studies for material discovery by applying inverse design strategy, mostly using the Best First Search (BFS) algorithm as the technical basis.^{35,36}

In this work, the inverse molecular design is conducted based on the VDS algorithm for its ability to escape from local traps. VDS is a well-known heuristic algorithm, which was originally

proposed by Kernighan and Lin in 1970s to solve traveling salesman problem and the graph partitioning problem.^{37,38} Recently, the VDS algorithm has been adopted to find the ground state of a spin glass.³⁹ The main idea of VDS is to perform a sequence of local move adaptively and select the next move in a greedy way. In our study, a local move is defined to modify the parent molecule in specific sites by selected substituent. The gain here refers to the changes of the C–H BDE after modification, which may be positive or negative. If there is a local move that increases gain, then a move with maximal gain is chosen. Otherwise, a move with minimal loss is selected. Local moves are not imposed to decrease the BDE, but allowing to climb out of a valley taking the direction of least resistance, which is a distinguishing feature of VDS in comparison with the BFS algorithm.

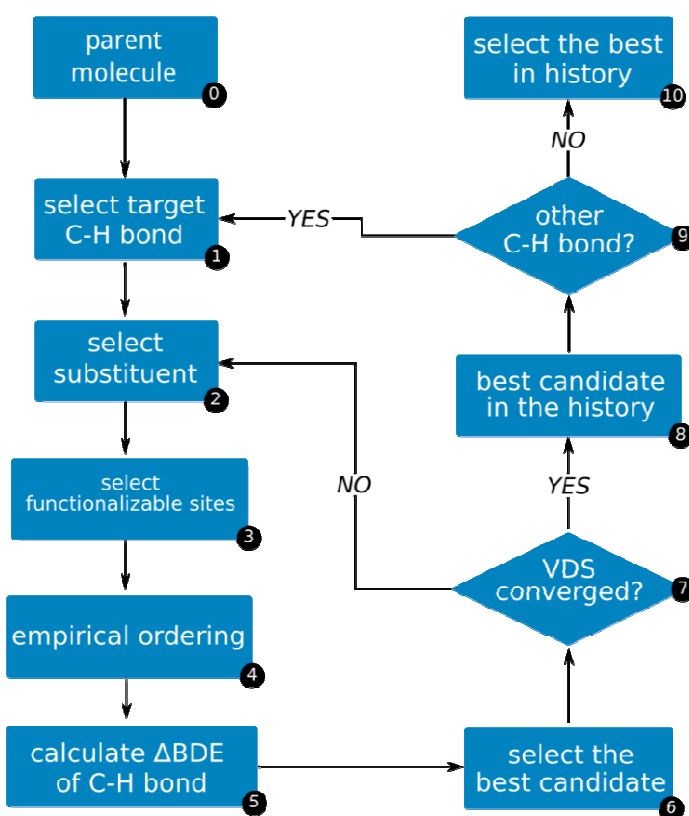


Figure 6. Flow chart of inverse design of optimal H-donor candidates.

The flowchart of inverse design of optimal H-donor candidates is illustrated in **Figure 6**. Selecting a starting molecule as the parent (step 0) and the BDE of one of its C–H bonds as the target (step 1), the parent molecule framework was modified at various functionalizable sites (step 3) by selected substituent from a predefined library (step 2, see **Figure 8** and discussion below for substituents definition). Based on a set of empirical rules (step 4, see discussion below for details), only five most promising candidates were kept for further DFT evaluations (step 5). The searching is proceeded in VDS scheme following the direction of lowering the target C–H BDE (step 6). VDS will be terminated after two failed attempts and the final structure is the best one in searching history (step 7 and 8). The searching may pursue another iteration if there is other C–H bond in starting molecule available for modification (step 9). The candidate with lowest C–H BDE in searching history is selected as the most promising H-donor (step 10).

3.3.2 Empirical rules for screening structures and selected substituents.

The major obstacle in our inverse design strategy is the huge number of candidate molecules demanding for DFT evaluations. For example, considering tetralin as the starting molecule, there are 15 substituents that may appear at any of the 8 different sites within its framework. If searching for 3 iterations, the number of possible candidates could be over 10^6 . The situation is actually more challenging, as some substituents can modify the molecule in a bidentate style and create new functionalizable sites.

However, from a chemical point of view, most candidates could be safely ruled out without further DFT evaluations. For example, if the substitution is far away from the central carbon

atom in target C–H bond, it is expected to cause no noticeable change to C–H BDE. By using tetralin as the parent molecule and methyl, phenyl, vinyl as the substituents, as evidenced from **Figure 7(a)**, there is sizable changes in C–H BDE only when the substitution occurs at the central atom or one bond away from that.

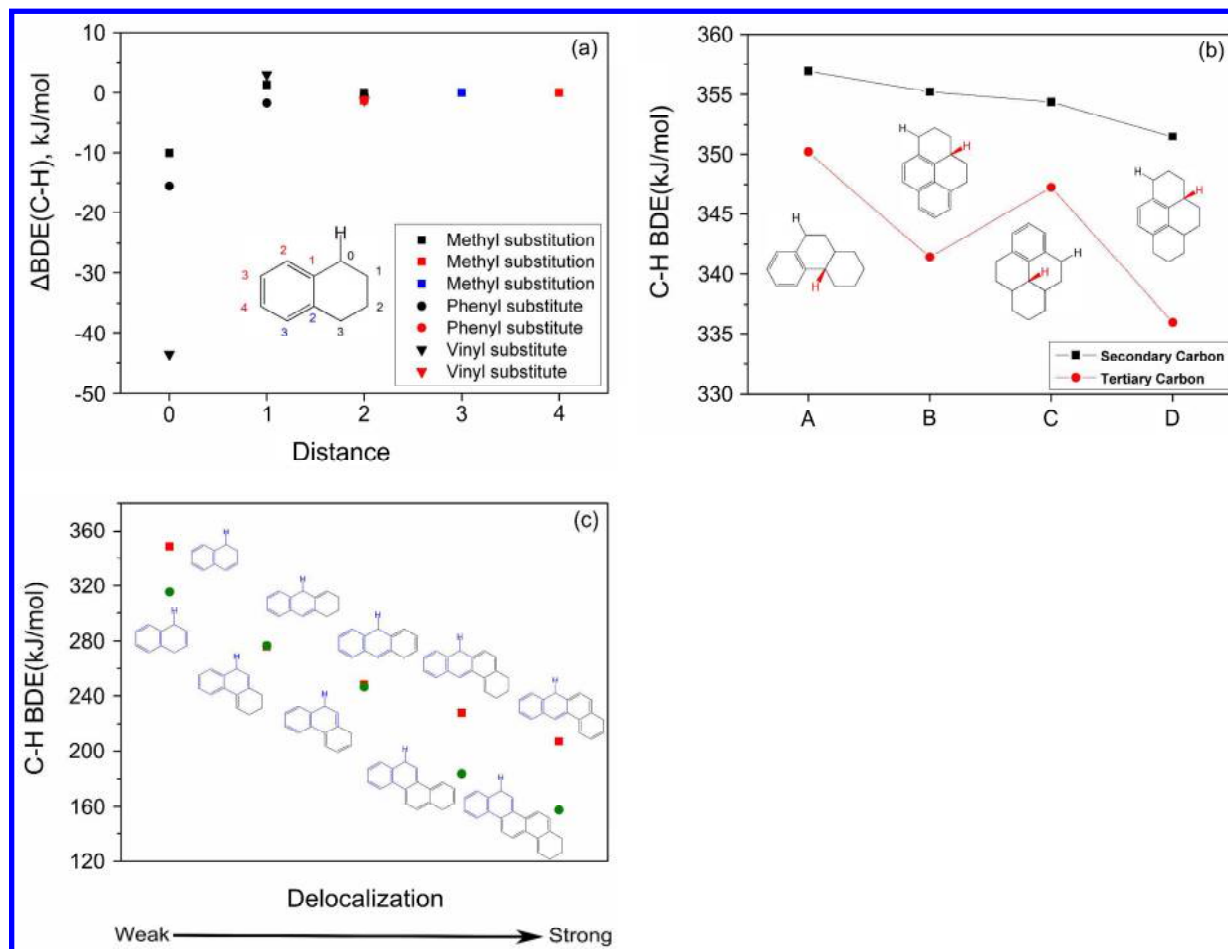


Figure 7. (a) Effects of different substituents at different sites on C–H BDE of tetralin. The target C–H bond is explicitly displayed and the center carbon atom is labeled as 0. The (topological) distance is the shortest number of chemical bonds from the center atom. (b) Relationship between $\text{C}_\alpha\text{--H}$ BDE and α carbon type. (c) BDE changes are affected by the size of

delocalization area. Parent molecules and substituents are highlighted in blue and black color, respectively.

To reduce computational time, we introduced an empirical ordering step in VDS flowchart (**Figure 6**) by applying three heuristic rules to guide molecular modifications. First, these rules utilize the most prominent chemical modifications that affecting C–H BDE, which are based on both chemical knowledge and our preliminary tests by a trial and error method. Second, applying these rules is sufficient to generate most of relevant model compounds of H-donor solvents derived from industrial plants. As mentioned above, the first rule is to favor the modification at the site that in low topological distance to the target carbon atom. The second rule is to favor high alkyl substitution for its tendency to weaken the C–H bond. **Figure 7(b)** illustrates the distinct difference in C–H BDEs for carbons in different substitution degree. The resulting difference is about 8-15 kJ/mol. The third rule is to favor the substitution that creates larger degree of conjugative resonance stabilization of the hydrogen abstracted radical. As exemplified in **Figure 7(c)**, parent molecule was modified in two different ways. The modification that has a larger resonant structure for radical will decrease the BDE faster. The last rule is to select a smaller substituent if possible, in order to make the structure has more chances to evolve before reaching the molecular size limit. New H-donors are efficiently screened and designed by applying those four rules defined above.

Figure 8 shows the substituent library for structural modification used in this work. Although there are plenty of aromatics with alkyl side-chains in coal liquefaction solvents^{40,41}, alkyl substituents are excluded for their inefficiency in reducing C–H BDE, as compared with alkenyl or methylene groups. Phenyl is another common group appearing in structures of coal

liquefaction solvents.^{42,43} Besides, several moieties in different size containing alkene groups are included in our library for bidentate substitution, as coal liquefaction solvents are mainly composed of aromatics with different number rings and arrangement.⁴⁴

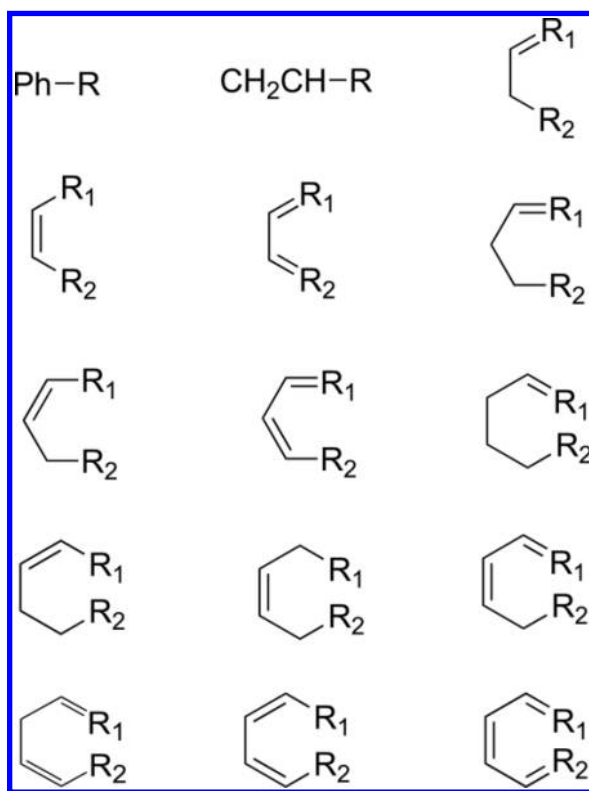


Figure 8. The library of substituents for structural modifications. R , R_1 , R_2 are the attaching points for structural modification.

3.3.3 Structure modification based on tetralin.

Tetralin is by far the most frequently used hydrogen-donor molecule in coal liquefaction studies. As shown in **Figure 9** we select tetralin as the starting molecule to demonstrate our inverse design strategy. In the first iteration, the tetralin molecule was extended to 3-ring after substitution to reduce $\text{C}_\alpha\text{-H}$ BDE. In the sibling nodes, indicated by C-H BDEs ($\text{X}_{3\text{D}}$ values), the most stable molecule is the one containing two alkenyl groups one bond away from the target

carbon atom, which will help to maximize delocalization of the corresponding radical. Similarly, the C–H bond can be further activated in an iterative manner by functionalization at appropriate sites with specific substituent. For tetralin, the searching terminated after 3 iterations when the molecule reaching size limit (20 carbon atoms). **Figure 10(a)** summarizes how C–H BDE evolves in searching along different iterations, as only the structures corresponding to parent nodes displayed for clarity. The BDE decreases 165.7 kJ/mol (in X_{3D}) after first two iterations, and then decreases 28.0 kJ/mol further in the next iteration. Judging from the trend as shown in **Figure 10(a)**, it looks like the BDE can be lowered further if searching continues, although the resulting molecule may be too large to be practically relevant. The searching tree for tetralin with C_β –H bond as the target shows similar trend, which is presented in ESI (**Figure S1-Figure S8**).

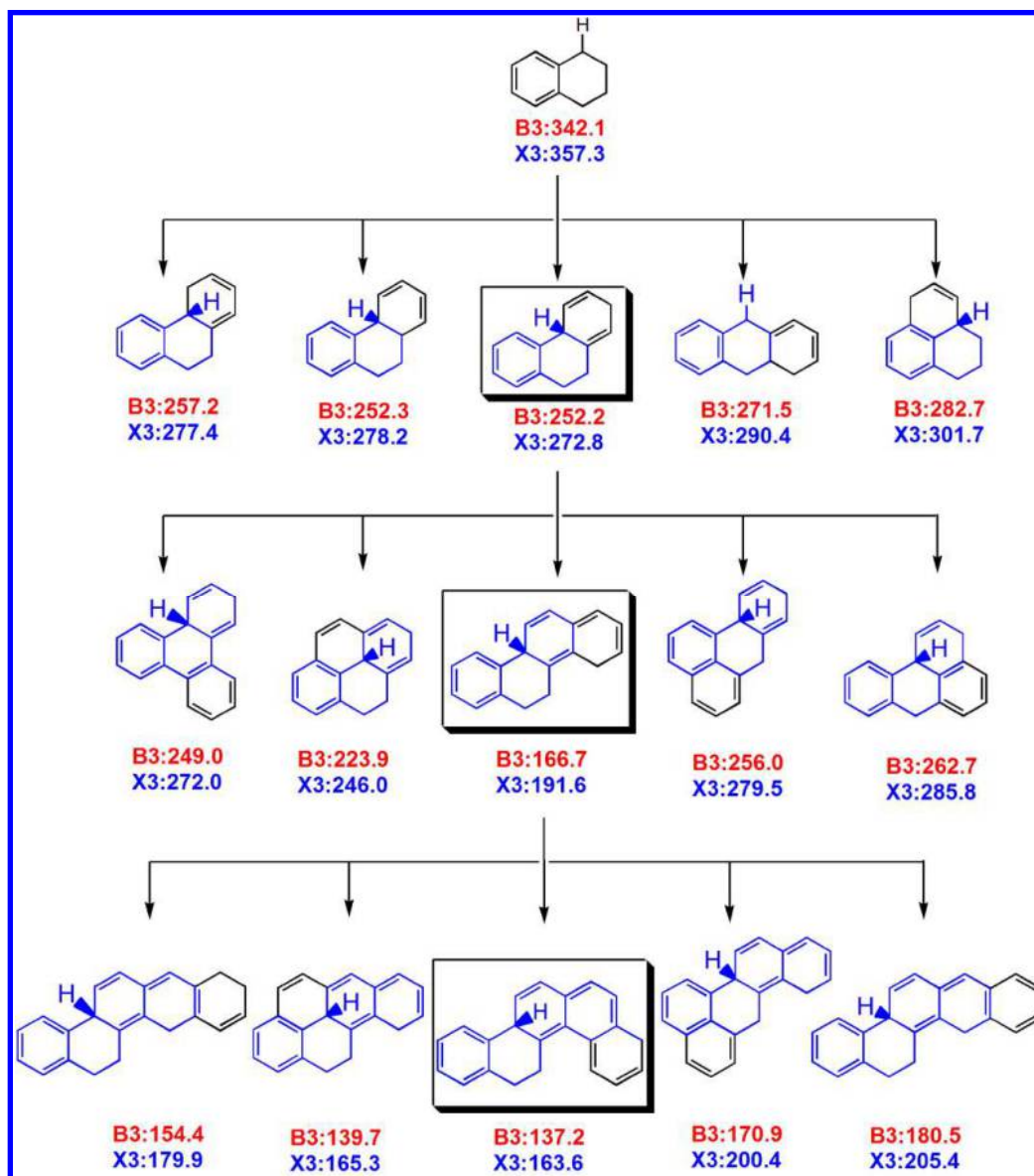


Figure 9. VDS tree for tetralin constructed during structure modifications. All values are reported in kJ/mol. Structures selected as parent molecules in previous iteration are highlighted in frame. Molecule fragments representing parent framework are displayed in blue. B3: BDE at B3LYP level. X3: corrected BDE using X_{3D} scheme. The searching is directed based on X3D values.

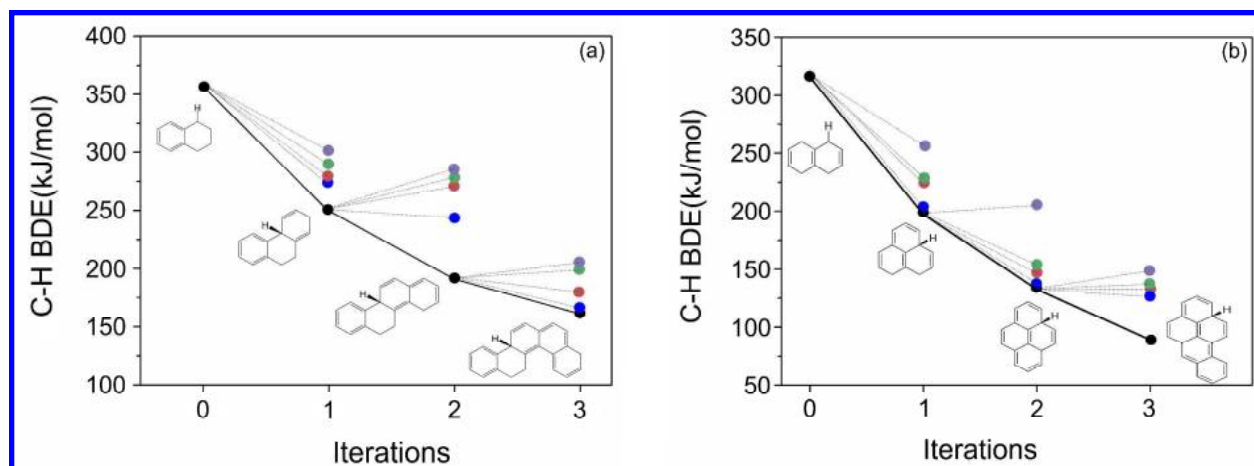


Figure 10. H-donor candidates for (a) tetralin and (b) isotetralin during VDS procedure. Molecules with higher BDEs than the minima in current iteration are omitted for clarity. BDEs were corrected using X_{3D} scheme.

3.3.4 Structure modifications based on cyclic olefins.

As a new development in hydrogen-donor molecules, Curtis et al.^{45,46,47} found that cyclic olefins show higher reactivity in releasing hydrogen than their conventional hydroaromatics analogues. It is interesting to see how to design better H-donors by using cyclic olefins as the starting structures.

As seen in **Figure 10(b)**, by using isotetralin as the root node, the C–H BDE decreases rather quickly. The BDE was lowered by over 225.6 kJ/mol after 3 iteration, about 31.9 kJ/mol lower than the case for tetralin. Other examples are presented in supporting materials.

3.4 Validation of the candidate H-donors on the activation barriers.

Our results show H-donors in starting structures can be modified in the direction of lowering C–H BDE. One may wonder if the modifications are really effective to lower activation barriers.

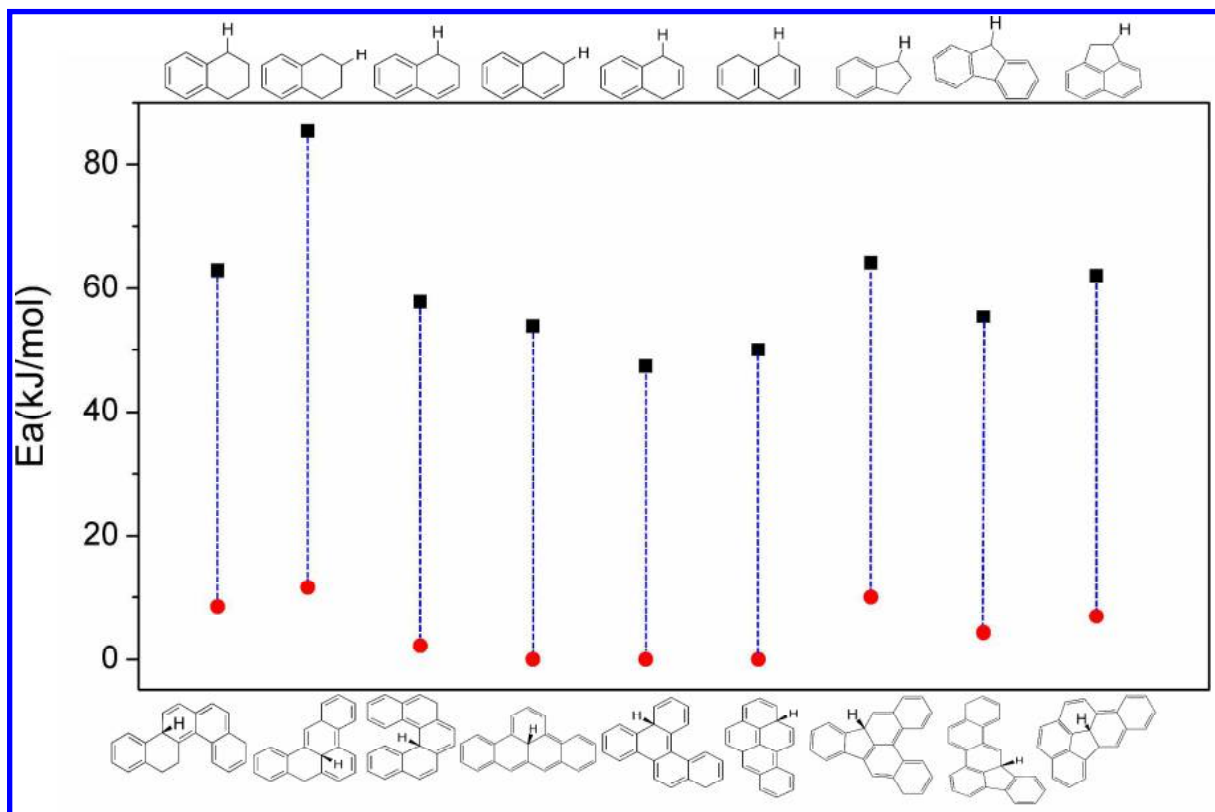


Figure 11. Activation barriers of H-donors before and after modifications. Values were reported in kJ/mol at B3LYP/6-311+G(d,p) level.

For all designed H-donors starting from different molecules, the activation barriers were obtained at B3LYP level by locating the transition states in the concerted mechanism. As show in **Figure 11**, the activation barriers of C–H bond dissociation for starting structures, are in the range of 47 ~ 86 kJ/mol, while the values of the corresponding candidate H-donors are

significantly lowered to below 12 kJ/mol, which means the hydrogen transfer reaction would be extremely easy.

Our inverse molecular design approach set up a framework for systematically improving donation ability of a H-donor by structural modifications. Besides, it can create a large set of candidate H-donors allowing the designer to choose the appropriate H-donors prior to expensive experiment evaluations, which fully meets our design goals.

4. Concluding remarks

In this work, we present an inverse design approach for systematically constructing promising H-donor candidates in direct coal liquefaction based on DFT calculations. Important thermodynamic quantities such as BDEs are obtained by using the newly developed X_{3D} scheme for obtaining high accuracy.

The hydrogen donation mechanism of solvent in direct coal liquefaction has been first explored in details by using common model compounds of H-donors and coal radicals, respectively. The hydrogen transfer from H-donors to coal free radicals is more likely to proceed via a concerted mechanism assisted by coal radicals, as the intrinsic reaction barriers are fairly below 80 kJ/mol for all studied model compounds.

To break the bottleneck of computational demanding in molecule design of optimal H-donor candidates, a linear scaling relation between C–H BDEs and activation barriers was successfully established. Then, the inverse design scheme for seeking optimal H-donors is proposed by using C–H BDE as the descriptor based on the variable depth search algorithm. The molecular searching space for structure modification was reduced by a set of empirical rules obtained from chemical intuition and test calculations. Finally, several illustrative examples are

given to demonstrate how the inverse design approach is applied to make starting molecule evolve in the direction of higher hydrogen-donor ability. The promising H-donor candidates obtained were further validated by locating the transition states in concerted pathway. Compared with their parent molecules, the activation barriers of candidates are significantly lowered to below 12 kJ/mol, which clearly show the effectiveness of our inverse molecular design approach.

Our results pave the way toward the rational design of candidate H-donors promising for improving the yields of the liquid products from coal under mild conditions. Obviously, the rational design framework is requiring continuous improvement. As this study is limited to theoretical evaluation, it is solely based on C–H BDEs of H-donors as it is simple to carry out the inverse search. We are aware that many practically important factors for screening H-donors are neglected in current version, such as the thermodynamic stability, the concentration of donatable hydrogen, and solubility of coal and liquefaction products in H-donor. A future work will endeavor to find more representative descriptors beyond C–H BDEs in designing the ideal H-donors.

Associated content

Supporting information

Experimental and calculated C–H BDEs by different methods (Table S1), different kinds of compounds in coal liquefaction solvents (Scheme S1) and VDS trees for tetralin and its derivatives constructed during structure modifications (Figure S1-S8) are provided in the Supporting Information.

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Notes

[§]These authors contributed equally to this work. All authors declare no competing financial interests.

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